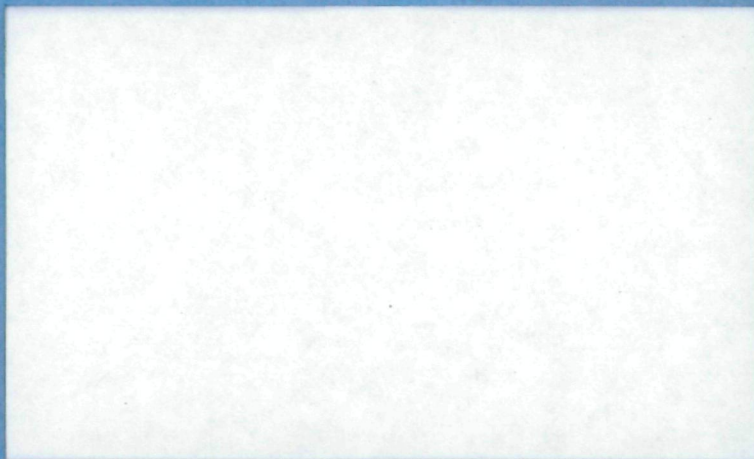


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Bismaleimide Resins for Flame Resistant
Honeycomb Sandwich Panels.

by

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A B S T R A C T

Bismaleimide resins are prime candidates for non-flammable aircraft interior panels. Three resin types with different structures and processing characteristics were formulated. Resin M 751 was used to fabricate 100 kg of glass fabric prepregs which were delivered to NASA-Ames Research Center. 10 kg of the neat resin were also delivered. Glass fabric prepregs were used for the preparation of face sheets for honeycomb sandwich panels. Prepreg characteristics and curing cycles for laminate fabrication are provided.

In contrast to M751 resin which is processable from NMP Solvent, a resin modification which is soluble in low boiling solvents was developed. This resin, coded M 756, should have been used to develop a Nomex-bismaleimide honeycomb core. Impregnation of prime cured honeycombs is not possible from low boiling solvents like acetone or tetrahydrofuran which were tried for the M 756 resin. Two other resins were used successfully from low boiling/high boiling solvent combinations for the development of B-stage Nomex-polybismaleimide honeycomb core.

In order to advance beyond the current solvent resin technology for fibre and fabric impregnation, a hot melt solvent-less resin system was prepared, characterized and delivered to NASA-Ames Research Center. Preliminary tests were performed to develop a "wet bonding process" for the fabrication of advanced sandwich honeycomb panels by use of polybismaleimide glass fabric face sheets and polybismaleimide Nomex honeycomb core. B-stage material was used for both the core and the face sheet, providing flatwise tensile properties equivalent to those obtained by the state-of-the-art 3-step process which includes an epoxy adhesive resin.

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BISMALEIMIDE RESINS FOR FLAME RESISTANT
HONEYCOMB SANDWICH PANELS

I INTRODUCTION :

There exist a number of synthetic routes to prepare new and improved high temperature resistant polymeric materials that are flame resistant as a consequence of their polymer composition. Many of the new thermally stable polymers developed during the last 10 years have found many applications in the form of films, fibres and moulding compounds. During the last five years increased attention has been paid to the use of high temperature polymers in combination with glass, carbon, boron and aramid fibres for the development of advanced composites for structural components to be used under unusual environmental conditions. The fabrication of composites, by using morphologically linear thermoplastic poly(imides), poly(phenylquinoxalines), poly(benzimidazols) and the like, is very complicated due to the high melting and/or glass transition temperatures. Solubility in high boiling polar solvents is the only tool for processability.

To overcome processing disadvantages many different synthetic approaches have been developed for thermosetting non flammable high temperature resins. The most popular concept is based on bismaleimides which undergo thermal polymerization at temperatures between 150 - 400° C (1). The great advantage of this approach is that low molecular weight imide prepolymers endcapped with reactive maleimide rings are polymerized into highly cross-linked thermally stable polyimides without the evolution of by-products. Another type of thermosetting polyimide resin was developed by TRW-System (2). The terminating nadic imide endgroups undergo pyrolytic polymerization during cure. More recently polyimide prepolymers with acetylene endgroups were developed (3). These resins cure by a cyclotrimerization reaction forming a totally aromatic polymer.

Maleimide-type resins :

Bismaleimides are prepared by reacting an aromatic diamino-compound with maleic acid anhydride followed by cyclodehydration (4). The resulting

bismaleimide monomers can be cured by simply heating to temperatures of 180 - 240^o C, thus forming a dense, insoluble unmeltable polymer network (1,5,6). The applicability of these resins is somewhat limited because of their brittleness and low impact resistance as a consequence of the low elongation at break of the neat resin. A technical resin modification with improved flow properties and somewhat better extensibility is available from Rhone-Poulenc under the trademark Kerimid 601 (Fig.1) (7). The resin is made by reacting a bismaleimide with an aromatic diamino-compound to form a prepolymer which is meltable (80 - 105^o C) and soluble. Prepregs can be fabricated via NMP-solution techniques. Laminates and honeycomb sandwich panels can be successfully fabricated by using either high pressure techniques for thick laminates or low pressure autoclave techniques for honeycomb sandwich panels.

Processing of Bismaleimide Resins :

The choice of the processing technology for the fabrication of composites, i.e. laminates and honeycomb sandwich panels, depends on the flow properties and solubility characteristics of the resin. Liquid or liquifiable binders need no solvent for impregnation (Fig.2). Other Bismaleimide Resins like Kerimid 601, which have higher prepolymer molecular weights, need to be dissolved for fibre or fabric impregnation. As a consequence of the very low prepolymer molecular weight, solventless resins show extremely good flow properties and are therefore considered for low pressure autoclave moulding (20 - 50 psi) (8) and for filament winding (9). Kerimid 601 and similar resin types need N-methylpyrrolidone as a solvent for prepregging. Residual solvent in the prepregs is necessary to obtain tackiness and drape. It has to be considered that residual solvent also remains in the moulded laminate and causes thermoplastic failure at high temperatures (10) under stress.

Aircraft Interior Panels :

Under NASA-sponsorship the flammability characteristics of aircraft interior composites have been evaluated (11). It was the purpose of this programme to assess the relative flammability and thermomechanical properties of some typical state-of-the-art and candidate experimental aircraft interior composite panels. The outcome of this evaluation was that sandwich panels prepared with bismaleimide type resins are the most promising from the flammability point of view.

As compared with epoxy and phenolic type resins the flatwise tensile strength

in the finished sandwich panel is low and does not reach industrial requirements when bismaleimide resins are used. Also the processing technology is complicated and expensive and has to be improved. High flatwise tensile strength (ASTM - C307) in honeycomb sandwich panels is obtained when epoxy resins are used either as a film adhesive between the face sheet and the honeycomb, or as a resin-rich (60 % by weight) prepreg. Satisfactory bondings are the result of optimum resin flow and the formation of a good glue line.

Advanced, nonflammable honeycomb sandwich panels, as evaluated by NASA-AMES, are fabricated from resin (K 601) poor prepregs. The combination of the following facts :

- a) resin poor prepreg
- b) low flow properties of K 601 as compared with epoxy
- c) low resin tensile strength

are responsible for the low flatwise tensile properties.

Besides the low bonding capability of K 601 glass-fabric prepregs to the honeycomb, the overall processing is not satisfactory. Additional R & D work is therefore necessary to improve both the processing and the properties of advanced aircraft interior composite panels. The proposed research and the objectives of this programme are as follows :

Proposed Research :

- 1) Development, preparation, characterization and delivery of 1 kg polybismaleimide resin Code A to NASA-AMES.

This resin should be soluble in low boiling solvents to provide improved processability.

- 2) Preparation, characterization of maleimide resin Code M 751.

2.1. Delivery of 10 kg to NASA-AMES.

2.2. Delivery of 100 kg of glass fabric prepreg with the resin Code M 751. The 100 kg prepregs have to be delivered in two different forms :

- 2.2a. 50 kg dry form (rest solvent content very low). These 50 kg will be fabricated by using glass fabric style 181.
 - 2.2b. 50 kg tacky form (rest solvent content high). These 50 kg will be fabricated by using glass fabric style 120.
- 3) Preparation, characterization and delivery of 1 kg maleimide-resin code C (this resin is a hot melt resin that can be processed without any solvent) to NASA-AMES.

Programme Objectives :

of the proposed research are:

- Polybismaleimide-Nomex Paper Honeycombs are not available. It is proposed to develop basically the possibilities of fabricating such honeycombs by using commercially available expanded honeycombs (nodes of the honeycomb bonded together with an epoxy adhesive) and a bismaleimide resin which is soluble in low boiling solvents.
- to develop a B-stage bismaleimide honeycomb core for improved processability.
- to evaluate the flatwise-tensile properties obtainable in honeycomb sandwich composites with bismaleimide resin face sheets.

Three candidate resins will be used :

Resin A (same as used for honeycomb impregnation)

Resin B : Code M 751

Resin C : hot melt bismaleimide resin

- The main objective of this programme is to overcome the state-of-the-art three step process for advanced composite fabrication by using B-stage honeycomb core (Nomex/Polybismaleimide) and high flow resin fabric face sheets.

II RESINS INVESTIGATED

During the course of this work three resin types have to be considered to be used for non-flammable aircraft interiors. The main disadvantage of the commercially available resin Kerimid 601 is the limited shelf life of the prepreg material fabricated from NMP-solution. Thus the flow properties are decreased to nearly zero when it is stored at room temperature for three to four days. The loss of flow properties means the loss of the binding capability to the honeycomb core and consequently low flatwise tensile properties are obtainable.

Resin M 751 :

Recently Technochemie developed a new chemical approach to overcome the aforementioned disadvantages. The chemistry of the new resin Code M 751 is outlined in Figure 3. m-Maleimidobenzoic acid chloride (m-MIC) is reacted with an aromatic diamino compound in such a way that the molar proportion of difunctional amine to the acid halide is between 1:2 and 1:1. The resulting polybismaleimide prepolymer consists, depending on the molar reaction proportion of the reactants, of a mixture of the two compounds III and IV (Fig.3). The polymerization of the resin can be accomplished by simply heating the resin to temperatures between 180 - 240° C. The polymerization proceeds controlled in such a way that first the free amino groups react with the double bonds of the maleimide forming a linear prepolymer, which then crosslinks by a free radical polyaddition mechanism. The advantage of this resin system is that a controlled prepolymer molecular weight can be obtained reproducibly by simply selecting the molar composition of the m-MIC and 4,4'-diamino-diphenylmethane (1:0,7). The resin is meltable (see DSC, Fig. 4) at 120 - 135° C, forming a high viscosity melt. The resin is soluble in NMP (N-methylpyrrolidone), DMAC (Dimethylacetamide) and DMAC-THF (tetra-hydrofuran) mixtures from which it can be used to impregnate glass fabrics (prepregs).

This resin formulation, coded M 751, was selected for the fabrication of improved glass fabric face sheets. According to the requirements of this contract (NASW - 3081) the following items had to be delivered to

NASA-Ames Research Center :

a) 10 kg of Resin M 751.

This material was produced on a pilot plant scale, batch no: T4 and was delivered to NASA-Ames.

b) 50 kg of dry prepreg fabricated using fabric style US 181 and Resin M 751.

c) 50 kg of tacky prepreg using fabric style US 120 and resin M 751.

To fabricate 100 kg of glass fabric prepregs a 60 kg batch of resin M 751 (Batch No. T8) was produced on a pilot plant scale. The material was then dissolved in NMP and was delivered to the prepreg company as a 47% by weight solution (Batch T9).

M 751 Resin Properties :

The properties which characterize the M 751 resin are summarized in Table 1. A comparison is made between a typical laboratory batch (LB), the 10 kg delivery to NASA (batch T4) and the 60 kg batch (T8).

Melting Behaviour :

As a quality control the melting behaviour of the resin is tested by using the Du Pont Thermal Analyser 900 in combination with the DSC-unit. Figure 6 presents the DSC-trace of the neat uncured resin (batch T8). As compared with the 10 kg delivery of December (batch T4) (Fig.5), the onset temperature (T_{os}) and the peak temperature (T_{max}) are lower, but higher than those of the typical laboratory batch (LB). The scale up of the laboratory procedure for the resin fabrication can lead to a batch to batch variation of the melting behaviour. However the variations obtained for all batches tested (Table 1) are not significant for the use as a laminating resin.

Density of the Neat Cured Resin :

The density of the cured resin is used to test the polymerization behaviour and the flow properties of each resin batch. The procedure to prepare a dense, void free, transparent resin disc (thickness 1 - 2 mm) is given below :

Tooling : heated platen press

- 1) Preheat mould parts or platen press to 180° C.
- 2) Preform the resin powder at room temperature at $300 - 400 \text{ kg/cm}^2$.
- 3) Add the preformed M 751-pill to the heated mould or between the platen press.
- 4) Heat the preformed M 751-pill for 10 minutes at 180° C.
- 5) Apply pressure ($20 - 50 \text{ kg/cm}^2$). (The pressure should be applied slowly to prevent squeeze out of resin).
- 6) Hold for 5 minutes at 180° C.
- 7) Heat to 220° C and cure for one hour.
- 8) Post cure for 15 hours at $210 - 220^{\circ}$ C.

If no mould to preform M751-powder is available, the powder can be moulded between aluminium foils. By use of this procedure a dense, void free, neat resin sample can be cut from the centre of the disc, which is transparent and useful for the density measurements. The ability to obtain a dense transparent moulded neat resin shows that good flow properties are to be considered. These tests also showed that the resin is useful for transfer moulding. The densities obtained for the different batches are between $1,29 - 1,32 \text{ g/cm}^3$ (Table 1.)

Viscosity-time Profile :

The usual prepregging technology is based on low viscosity impregnation varnishes to apply resin onto the reinforcement. Drying of the prepreg is necessary to strip off the solvent. Because of the chemical reactivity many Bismaleimide-type resins tend to advance in solution leading to increased solution viscosities. The advancement depends on the temperature and the solvent system used. For the resin system M751 the preferred solvent is NMP (N-methylpyrrolidone), but DMAC (Dimethylacetamide) or DMF

Table 1: M751 Resin Properties

Property	BATCH NO.				
	LB	T ₂	T ₄	T ₈	T ₉
T _{os} (DSC, 10°C/MIN) [°C]	124	132	135	127, 5	---
T _{max} (DSC, 10°C/MIN) [°C]	137	146	149, 5	142	---
Density ¹ g/cm ³	---	1, 32	1, 31	1, 29	---
T _{D10} (TGA, 10°C/MIN)	---	---	---	400	---
Solution viscosity ² -- ageing η in [cst] η 5 d [cst] η 10 d [cst] η 20 d [cst]	NMP 50%	NMP 50%	NMP 50%	NMP 50%	NMP 47%
	470 - 560	411	295	422	353
	580 - 705	510	380	680	525
	735 - 890	645	465	960	710
	1220 - 1500	740	680	1500	1120

1 Density of cured Resin

2 Ageing temperature 20°C

T_{os} = onset temperature of DSC - peak

T_{max} = temperature of DSC - peak maximum

T_{D10} = Decomposition temperature from
TGA - curve. Temperature at which
10% weight loss has occurred,
heating rate 10°C /Minute

(Dimethylformamide) can be used as well. Figure 7 provides the viscosity time profiles for the M751 resin batches T4 and T8. Batch T8 was measured in all the three solvents mentioned above. For 50% by weight solutions DMF gave the lowest viscosity and NMP the highest. All the viscosity-time profiles obtained are typical for the resin M751.

In Figure 7 the viscosity profile of a 47% by weight solution of resin T8 dissolved in NMP is provided and is coded T9. This is the solution which was prepared from Batch T8 resin and delivered to the prepreg company to fabricate the 100 kg glass fabric prepregs for NASA-Ames. This solution was aged at two different temperatures.

- At room temperature to compare with other batches.
- At 4⁰ C, which is the cool room temperature of the prepreg company.

As was to be expected, at low temperature (4⁰C) only a slow viscosity increase upon ageing is obtained.

At this point it is necessary to consider a glass fabric prepreg as a resin solution because of the rest solvent content of 2 - 10 % by weight. Therefore it is clear that advancing of the resin will occur upon ageing of the prepreg even at room temperature, and simultaneously will lead to a loss of flow properties. From this point of view resins that show viscosity stable impregnation solutions will produce prepregs with improved storage life. To demonstrate this behaviour further a comparison between M751 resin and Kerimid 601 is presented in Figure 8. The starting viscosity for all 50 % solutions, including K 601, is in the range of 230 - 420 cstokes. K 601 solution shows a constant viscosity increase with time and reaches 10.000 cstokes after 20 days. In contrast M751 resin solutions stabilise at a viscosity of about 700 - 800 cstokes after 20 days.

M 751 Prepregs :

Drying Curves for M751/181 - Prepregs

The typical laboratory procedure to prepare prepregs consists of passing dried glass cloth through the 40 - 50% by weight solution of the M751 Resin and removal of excess resin by passing the impregnate between a pair of steel rollers. To adjust a specific rest solvent content the prepregs

are dried in a circulating air oven. The rest solvent content is a function of the drying temperature and the drying time used. Figures 9 and 10 show the drying curves for M751/181 - prepregs, prepared from NMP and DMAC solutions, at various drying temperatures.

As was to be expected, high temperatures are necessary to adjust low rest solvent content in the prepregs prepared from NMP. For moulding thick laminates a very low solvent content is necessary to obtain good high temperature mechanical properties.

If we compare the prepreg quality for the 181-style material of the prepregger (5% rest solvent content) with the experimentally determined drying curves, we can see that drying for 15 minutes at 140^o C in a circulating air oven will provide the same rest solvent content as obtained by the prepreg manufacturer.

Prepreg Fabrication :

According to contract NASW-3081 two types of glass fabric prepregs from resin M 751 had to be fabricated and delivered to NASA-Ames Research Center.

- A) 50 kg from glass fabric US-style 181, Resin content around 30 - 35 % by weight, rest solvent content: as low as possible to produce around 3 - 5 % by weight.
- B) 50 kg from glass fabric US-style 120, Resin content around 35% by weight, rest solvent content around 15 % by weight to obtain drape and tack.

For this purpose a 47% by weight solution (120 kg) of the resin in NMP was prepared by Technochemie and delivered to the prepreg company (Firma August Krempel, 7143 Vaihingen/Enz 2 - Enzvaihingen, Postfach 240, Bundesrepublik Deutschland). Both prepreg types were produced using standard industrial prepregging equipment on March 13th, 1978.

The following prepreg properties were obtained :

Prepreg GHH 3006 (this is the glass fabric style 181 material)

Resin M751

Prepreg Area Weight	467 - 478 g/m ²
Glass fabric weight	290 g/m ²
Resin Content (1)	37,9 - 39,3 % by weight
Solvent content (2) (loss on drying 10 minutes, 160° C)	2,4 - 2,7 % by weight
Solvent content (3) (loss on drying 2 hours, 210° C)	5,1 - 5,3 % by weight
Flow (4)	16 - 20 % by weight

Prepreg GHH 1007 (this is the glass fabric style 120 material)

Prepreg Area weight	163,5 g/m ²
Glass fabric weight	103,3 g/m ²
Resin Content (1)	36,8 % by weight
Solvent Content (2)	17,7 % by weight
Flow (5)	20,4 % by weight

- (1) Resin content = Dry resin and Rest solvent
- (2) As determined by the prepregger
- (3) As determined by Technochemie
- (4) 6 layers of prepregs, pressure 20 kg/cm², temperature 170° C,
size 7,5 x 7,5 cm.
- (5) 10 layers of prepreg, pressure 20 kg/cm², temperature 170° C,
size 7,5 x 7,5 cm.

At the prepregger the solvent content is usually determined by drying the prepreg for 10 minutes at 160° C. But it is well known that higher temperatures are necessary to strip off all the solvent retained. The loss on drying at our laboratory is determined by drying the prepregs at 210° C for 2 hours in a circulating air oven.

The prepreg materials specified above have been delivered to NASA-Ames Research Center on March 23, 1978.

Curing Cycle for M751/181 - Laminates:

The following curing cycle was used to prepare a 10 layer (10 x 10 cm) laminate from prepregs fabricated by the prepregger.

Tooling: heated platen press

- 1) Preheat platen press to 170^o C.
- 2) Insert a stack of 10 layers of M751/181 prepregs between aluminium foils into the press.
- 3) Kiss contact for one minute.
- 4) Apply pressure of 20 to 40 kg/cm².
- 5) Hold temperature and pressure for two hours.
- 6) Cool to room temperature.
- 7) Post cure for 15 hours at 210^o C.

The following room temperature mechanical properties of the laminate are obtained. The flash (squeeze out) was 5% by weight.

Laminate Properties : (M751/181 - 10 Layer Laminate)

Laminate thickness	2,35 mm
Resin content	32 % by weight
Density	1,88 g/cm ³
Flexural strength (1)	556 N. mm ⁻²
Flexural modulus	23,4 KN. mm ⁻²
ILSS (2)	53 N. mm ⁻²

(1) Span to depth ratio 16:1 (ASTM D 790 - 66)

(2) Span to depth ratio 5:1

Thermal gravimetric stability of M751 - Resin

The TGA-curve for the neat M751 - Resin (batch T8) is shown in Figure 11. The sample investigated was moulded as described for the density sample preparation. For comparison the TGA-curve of the resin flash obtained from the moulded laminate is also shown (Figure 11). It can be seen that the TGA break of the material that has been in contact with the solvent

N-Methylpyrrolidone occurs at lower temperatures. Also the char yield is lower. This example again shows that processing of high temperature non-flammable resins by using high boiling solvents has to be done very carefully to prevent high residual solvent in the laminate. For thin face sheets this phenomenon is not so critical because post drying of the cured face sheet can provide a low rest solvent content. Therefore the following curing procedure for the fabrication of M751/181 preregs is recommended :

- 1) Cure face sheet for 2 hours at 170°C at a pressure of 7 kg/cm^2 between aluminium plates (mould release).
- 2) Post cure for 15 hours at 210°C in a circulating air oven.

This cycle is used by Technochemie to cure M751/181 prepreg face sheets.

M756 - Resin (resin code A)

To obtain honeycomb sandwich panels with improved non-flammability properties it was intended to impregnate prime cured, expanded polyamide (nomex) honeycomb cores with bismaleimide resin. Low boiling solvents are preferably used and the core can be dip-coated with resin solution and air dried. Stepwise increase of the temperature can then evaporate entrapped solvent and promote prepolymerization. The B-stage honeycomb core can then be press or autoclave cured by simultaneously bonding the face sheets. This so-called "wet bonding" could improve the mechanical properties of the finally cured sandwich. The state-of-the-art three step process for sandwich laminate fabrication can probably be overcome.

For this purpose it was necessary to develop a bismaleimide resin which is soluble in low boiling solvents like acetone, dioxane, tetrahydrofuran and mixtures thereof. Using the same chemical approach as for resin M751, a soluble resin was obtained by reacting m-maleimidobenzoic acid chloride with 4,4'-diaminodiphenylsulfone (Fig.12). This resin, coded M756, can be used as a 40 -- 50 % by weight solution in acetone, dioxane, tetrahydrofuran or NMP and DMAC for fibre, fabric and core impregnation. As a consequence of the low basic character of the free primary amino group, the solutions of this resin are extremely viscosity stable.

The first resin which was delivered to NASA-Ames (1kg) code M756-1, was prepared by reacting 1 mole of m-MIC with 0,6 moles of 4,4'-diaminodiphenylsulfone (DDS). In contrast to earlier laboratory batches this resin gave no stable solutions in acetone and tetrahydrofuran. The resin precipitated from the solution after standing for two days at room temperature. It was therefore necessary to reinvestigate the resin composition i.e. the molar ratio between m-MIC and DDS with respect to the solubility characteristics of the resin obtained. The change to a molar ratio of 1:0,65 (m-MIC : DDS) provided an acetone and tetrahydrofuran soluble material. 0,5 kg of this resin were delivered to NASA-Ames Research Center. This resin is coded M756-2.

Melting Behaviour :

The new composition M756-2 is a very low melting resin. Figure 13 shows the DSC-trace of this material indicating a melt transition between 81 and 92° C under controlled heating conditions. (10° C/min.)

Viscosity-time profile :

Viscosity-time profile (pot life) of a maleimide type resin is most important since impregnation of fibres and fabrics or a honeycomb core can be performed uniformly and reproducibly. According to the chemical composition of resin M756 an almost constant viscosity-time profile is obtained. (Figure 14). The resin can be processed from acetone (40% by weight solution) or tetrahydrofuran (50% by weight solution) as the low boiling solvent. Solvent combinations with DMAC or NMP can also be used.

Honeycomb core impregnation using Resin M756-2 (Preliminary tests)

Originally an attempt was made to prepare Bismaleimide Resin impregnated core panels by simply immersing the prime cured Nomex core in a 50 % by weight solution of M756-1 in acetone, followed by drying at temperatures up to 100° C in a circulating air oven. This procedure led to non-uniform impregnation and to a blistering off of the dry brittle B-stage resin because of the low film forming properties of the M756-acetone varnish. Several other solvent combinations were therefore tested and it was found that uniform impregnation could only be obtained by using a high boiling

solvent like DMAC in combination with tetrahydrofuran (THF). Solvent combinations of 5 - 10 % DMAC and 95 - 90 % THF are to be preferred. A resin concentration of 25 - 30% of the impregnation varnish provided a resin pick-up onto the honeycomb of 30 - 32 % by weight. Stepwise drying in a circulating air oven produced dry B-stage honeycomb material. The most important finding of these preliminary tests was that bismaleimide resin solutions in acetone or tetrahydrofuran cannot be used successfully for core impregnation. Small amounts of high boiling solvents like DMAC or NMP need to be present. It was therefore rational to consider a more economic resin formulation for use as impregnation varnish. (See Chapter 3, this report).

Hot melt Bismaleimide Resin (Resin Code C) :

The use of a solvent to fabricate laminates is usual in order to obtain uniform impregnation of the reinforcement. This technology is also common for epoxy prepreg systems. Very low boiling solvents like Acetone, Methyl-ethyl-ketone and the like are preferred because they can be stripped off easily in circulating air at moderate temperatures. The same technology has been used and still is in use for the fabrication of prepreps from bismaleimide resins (Kerimid 601). Due to the solubility characteristics of the resins, high boiling solvents such as DMF, DMAC, and NMP have to be used for prepregging. High temperatures are necessary for solvent removal and advancement of the resin occurs simultaneously. The great disadvantage which occurs is that a certain amount of the high boiling solvent remains in the moulded laminate resulting in low mechanical properties at high temperatures.

Solvent-less resin systems can help to overcome some of these problems. Recently the advantages of these resins when used for composites have been evaluated (10). The objective of this programme was to reinvestigate the possibilities of formulating a hot melt Bismaleimide type resin for a glass fabric prepreg to be used as face sheets for honeycomb sandwich panels. Again the state-of-the-art technology for sandwich panel fabrication (3-step process) has to be overcome.

On the basis of a new concept for bismaleimide resin formulation, a new

resin (Resin Code C of this report) has been designed. Figure 15 shows the viscosity-time profile and the gelation characteristics of this new resin. The resin as it is formulated, contains 6 % by weight of toluene which comes from the resin preparation process. Preliminary investigations to make glass fabric prepreps did show that in circulating air the remaining toluene can easily be stripped off to obtain a glass fabric prepreg with almost no residual solvent. One kilogram of this resin (Code H 795, batch M1268) has been delivered to NASA-Ames Research Center.

III. BISMALEIMIDE HONEYCOMB SANDWICH PANELS :

The development of bismaleimide resin type sandwich panels with improved mechanical performance (high flatwise tensile strength) and improved flammability characteristics within this programme consisted of the following steps :

- Preparation of face sheets from M 751/181 glass fabric preregs.
- Development of a laboratory procedure to fabricate B-staged Nomex-Bismaleimide resin (M756) honeycomb core.
- Evaluation of the flatwise tensile properties of composite panels fabricated from B-stage M751/181 face sheets and Nomex-Bismaleimide Resin honeycomb core by a one step curing process ("wet bonding process").

The state-of-the-art process to produce honeycomb sandwich panels from Bismaleimide resins consists of the following three step procedure :

- Cure of the face sheet prepreg material
- Preparation of the cured honeycomb core
- Bonding face sheets to the honeycomb core by use of an adhesive film (Autoclave or press curing).

For comparison two panels were fabricated using the state-of-the-art process (See panel No. S46 and S48, Table 2).

Base Line Panel Preparation :

The standard panels which were used for comparison were fabricated from M751/181 preregs (See materials specification, p.11 this report), Nomex HRH - 10 - 1/8 - 3,0 phenolic honeycomb core and AF126 - 2WT.06 adhesive film.

Face sheet cure :

The prepreg face sheets were cured by using the platen press method. A sandwich consisting of two M751/181 preregs and three Al-foil films

was placed into the preheated platen press (170°C) and kiss contact applied for 3 - 5 minutes. During this time residual solvent could be stripped off. After application of pressure (70 N/cm^2), the prepregs were cured for 2 hours at 170°C . After demoulding, the two face sheets obtained were post-cured for 15 hours at 210°C .

Baseline Panel Preparation. (Panels S46 and S48 - Table 2) Platen press curing (bonding) was also used to fabricate the baseline sandwich panels. The following build up : Al-film-M751/181 face sheet-AF126 adhesive film-Nomex-10 core-AF126 adhesive film-M751/181 face sheet-Al-film

was placed into the press, then kiss contact was applied and cured. (5 minutes 30°C , 10 minutes 50°C , 10 minutes 70°C , 15 minutes 90°C , 10 minutes 110°C and 1 hour 120°C). The properties of these panels are summarized in Table 2.

Nomex - Polybismaleimide honey comb core :

The preparation of B-stage Nomex-Polybismaleimide honeycombs was performed using the dip coating technique. The prime cured honeycombs were immersed in the solution of the bismaleimide resin. Excess resin solution was allowed to drop off and then the impregnate was dried in a circulating air oven. As was indicated earlier (This report p. 14) M756.2 resin from either acetone or tetrahydrofuran solution did not provide a uniform impregnation of the honeycomb core due to the insufficient film forming properties of these solutions. After drying off the solvent at temperatures around $70 - 100^{\circ}\text{C}$, the resin only formed a blistering brittle mass and no uniform coating. To prevent this phenomenon an attempt to improve the film forming properties was made by use of solvent combinations (low boiling, high boiling solvent combination). It turned out that 5 - 10 % of DMAC is useful for overcoming the difficulties mentioned above. As a follow up to these experiments the use of other bismaleimide type resins for honeycomb impregnation was tried. Because of the necessity of using a high boiling solvent it seemed rational to try out more economical resin formulations.

Recently Technochemie developed a new chemical approach for bismaleimide type resins (different to the chemical concept of Resins M751 and M756) with improved pot life as far as resin solution and prepreg alteration is

concerned. Specific resin formulations on the basis of this concept can be processed from DMAC/THF solvent combinations (resin M997) and from NMP/Methylenechloride solvent combinations (Resin M717). These two resins could be used successfully for the fabrication of sandwich panels with high flatwise tensile properties.

B-stage Honeycomb fabrication (Resin M997) :

A solution of M997 Resin was used to impregnate the honeycomb core, the varnish consisted of 34 % Resin M997, 62% Tetrahydrofurane and 4% DMAC, had a viscosity of 2,15 - 4,65 cSt at 100° F, was clear and stable (almost no increase in viscosity with time).

Prime cured NOMEX honeycombs (16 x 16 cm) were immersed in the bismaleimide varnish for one minute. Excess resin solution was allowed to drop back in to the resin reservoir and then the impregnate was dried in a circulating air oven (30 minutes at 20° C, 30 minutes at 50° C and 30 minutes at 100° C). The resin on the honeycombs prepared according to this procedure is in a very early stage of polymerization (A-stage). B-staging can be performed simply by heating to 140° C. It was of interest for this programme to know the compression strength of the core as a function of the B-staging time. Table 3 shows the compression strength of Nomex honeycombs impregnated with Bismaleimide resin as a function of B-staging time at 140° C. For comparison the equivalent values for prime cured and phenolic type honeycombs are given. As was to be expected the prime cured core had the lowest compression strength and the fully cured PBMI-core showed the highest value of all PBMI cores measured.

Table 2 : Properties of sandwich panels

Panel No.	Type Skins	Type Adhesive	Type Core	Type Cure	cured Density kg/m ³	Postcure after Bonding	Flatwise tensile strength No. Strength, kPa Avg (s.Dev.)	Compression Strength, kPa Avg (s.Dev.)
S43	M751 / 181 Prepreg	none	Nomex HRR10-1/8-3,0 Resin PBI M 714 (45,3 %) *	Press 10' 170° KK 110' 190° 87,3kPa	2,682	15h 210°	9 2142,7 (178)	2406,6 (486)
S46	M751 / 181 cured face sheet	AF 126-2WT.06	Nomex HRR10-1/8-3,0	Press, KK in 1h to 120° 1h 120°	2,712	none	9 2354,8 (60)	1924,5 (120)
S48	M751 / 181 cured face sheet	AF 126-2WT.06	Nomex HRR10-1/8-3,0	Press, KK in 1h to 120° 1h 120°	2,658	none	9 2179,5 (74)	1937,7 (25)
S53	M751 / 181 Prepreg	none	Nomex HRR10-1/8-3,0 Resin PBI M 997 (29,5 %) **	Press 1h 170° 4,4 kPa 2h 200° 4,4 kPa	2,214	none	9 614,6 (206)	1614,3 (47)
S54	M751 / 181 Prepreg	none	Nomex HRR10-1/8-3,0 Resin PBI M 997 (37,1 %) ***	Press 1h 170° 4,4 kPa 2h 200° 4,4 kPa	2,569	15h 210°	9 977,8 (163)	2065,5 (306)
S55	M751 / 181 Prepreg	none	Nomex HRR10-1/8-3,0 Resin PBI M 997 (37,9 %) **	Press 1h 170° 98,1kPa 2h 200° 98,1kPa	2,386	15h 210°	9 2069,4 (139)	2114,4 (213)
S56	M751 / 181 Prepreg	none	Nomex HRR10-1/8-3,0 Resin PBI M 997 (37,9 %) ***	Press 1h 170° 245 kPa 2h 200° 245 kPa	2,318	15h 210°	9 1932,7 (95)	2241,6 (55)
S57	M751 / 181 Prepreg	none	Nomex HRR10-1/8-3,0 Resin PBI M 997 (37,5 %) *	Press 10' 170° KK 13h 190° 87,3kPa	2,310	5h 210°	9 2027,7 (142)	1841,7 (114)

* A-stage NOMEX - PBI core, ** B-staged for 60 minutes at 140°C, *** B-staged for 80 minutes at 140°C, KK = kiss contact

Table 3 : Compression Strength of honeycomb cores.

Core Type	B-stage Time at Temperature (min) (° C)		Compression Strength (kPa)	S.Dev.
Prime cured NOMEX HRH 10 -1/8 -3,0	--		444,3	18,04
NOMEX HRH 10 Phenolic Resin	fully cured		1868,67 (2068,4 -x)	80,079
NOMEX HRH 10 PBMI Resin xx	20	140	701,10	94,64
"	40	140	913,76	84,11
"	60	140	892,07	82,50
"	80	140	762,24	72,38
"	420	210 (fully cured)	1256,27	201,88

(x) Value given by Hexcel

PBMI = Polybismaleimide Resin Code M997

(xx) Resin Content 32% by weight.

The commercial phenolic core type did show the highest compression strength (1868,67 kPa). It is of interest to note that the compression strength properties for the various B-stage PBMI cores do not vary significantly. Bearing in mind that the advancement of the resins does reduce the flow properties it seemed rational to use the A-stage PBMI-NOMEX core for the one shot "wet bonding" process to be used for sandwich panel fabrication.

Sandwich Panel Cure :

The main objective of this preliminary evaluative programme was to improve the flatwise tensile properties of advanced non-flammable honeycomb sandwich panels by bonding B-stage M751/181 prepregs to A- or B-stage NOMEX-PBMI-honeycomb cores by means of a so-called "wet bonding" process. The test panels (16 x 16 cm) for this evaluative work were fabricated using the platen press method. Details of the curing cycle (time, pressure) and the resulting panel properties are given in Table 2.

The interpretation of the flatwise tensile properties of all panels tested can be summarized as follows :

- Epoxy type adhesive films produced the highest flatwise tensile properties. The samples tested failed mainly in the phenolic type core at a value of 2,18 - 2,35 MPa which is the flatwise tensile strength of the core material. (Panel S46, S48 Table 2)
- B-stage M751/181 prepregs bonded to A-stage NOMEX HRH 10-1/8-30-PBMI-Resin core at a pressure of 85 kPa did produce flatwise tensile properties (2,0 - 2,1 MPa) quite similar to those of the epoxy film adhesive baseline panels. The samples tested failed mainly in the core. (Panels S43, S57 Table 2)
- B-stage M751/181 prepregs bonded to B-stage NOMEX HRH-10-1/8-30-PBMI-honeycombs did produce flatwise tensile properties which are dependent on the bonding pressure used. (Panels S53, S54, S55, S56). A moulding pressure of 98 - 245 kPa was sufficiently high to obtain a flatwise tensile properties of around 2,0 MPa. It has to be noted that all the samples tested did fail, mainly in the bond and not in the honeycomb core.

Conclusion :

Advanced non-flammable honeycomb sandwich panels with high flatwise tensile properties can be produced by bonding B-stage M751/181 glass fabric face sheets to A-stage Nomex-Polybismaleimide resin honeycomb core at low pressure (90 kPa) by a one shot "wet bonding" process. This technology offers the possibility of overcoming the expensive state-of-the-art processing technology and simultaneously increases some mechanical properties as compared with phenolic type honeycomb material.

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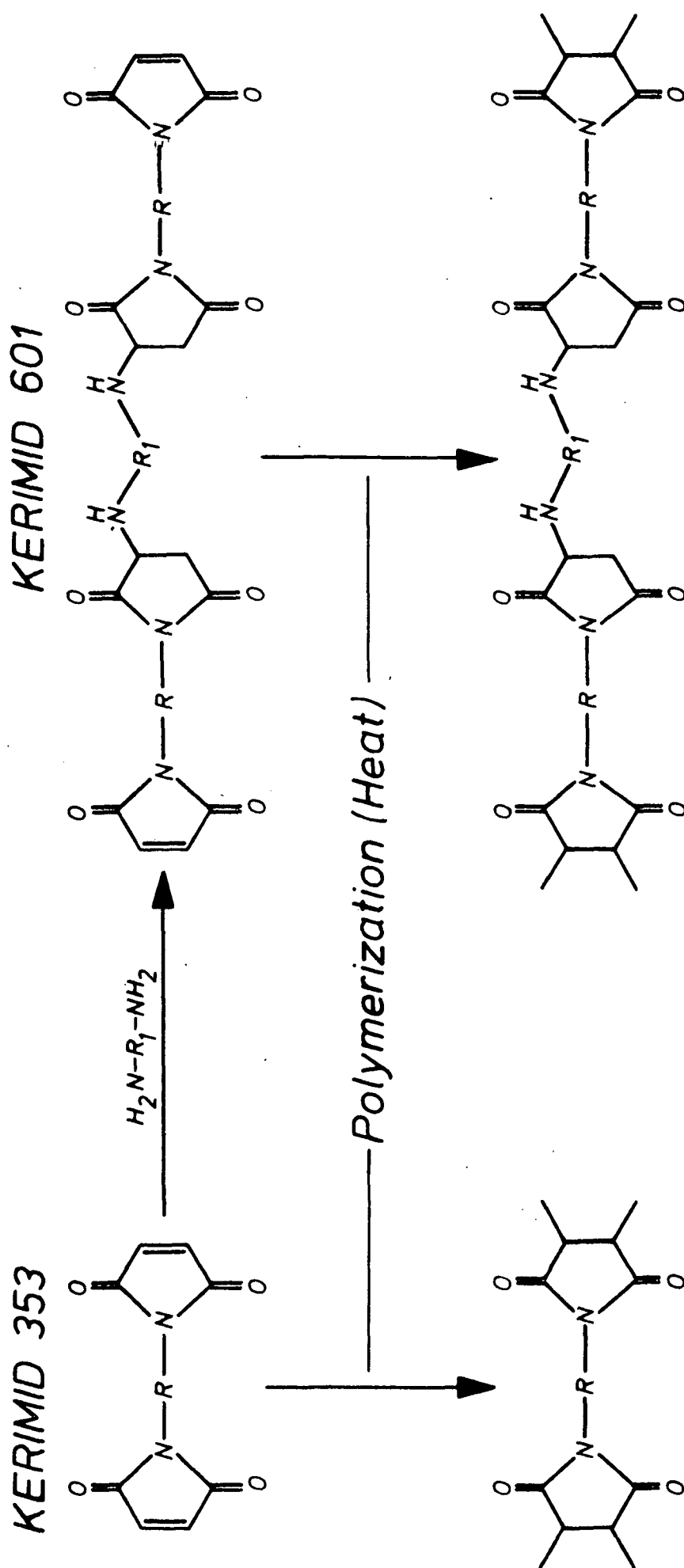


Figure 1: Maleimide resin chemistry

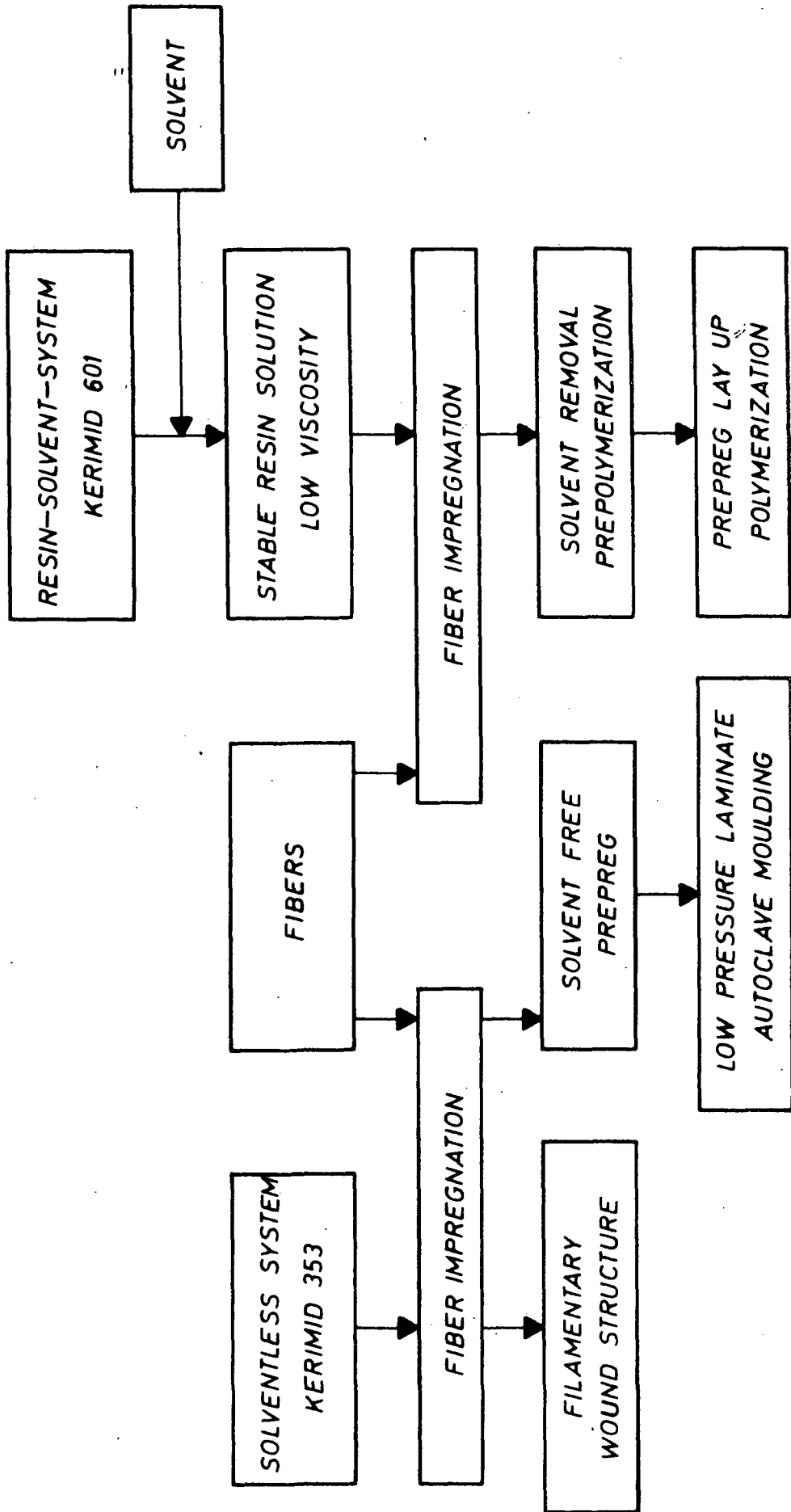


Figure 2: Processing of bismaleimide resins

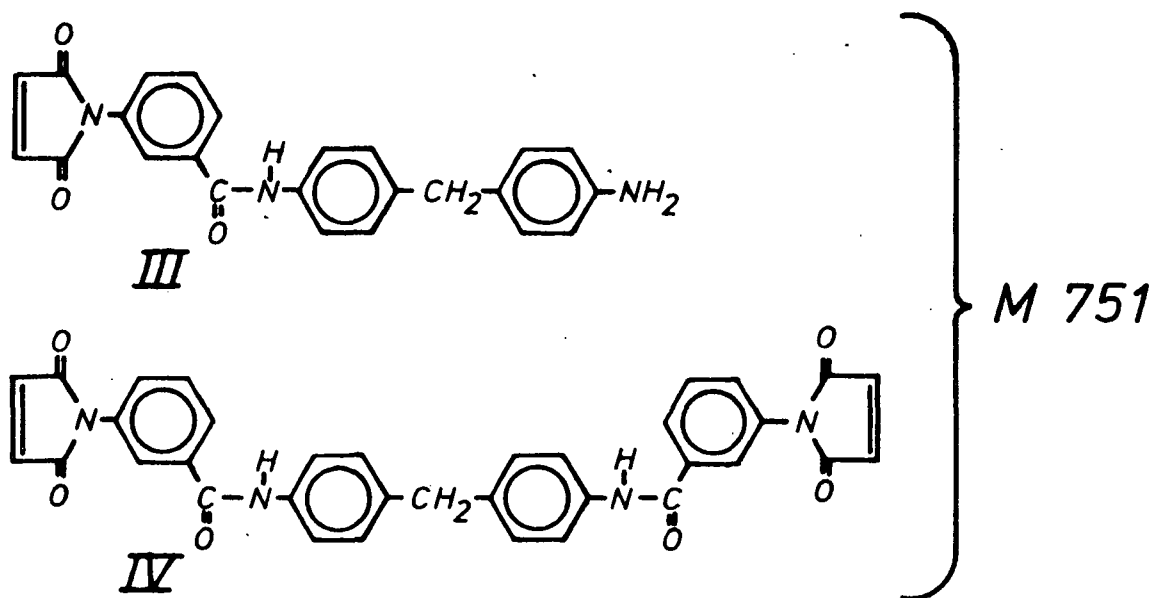
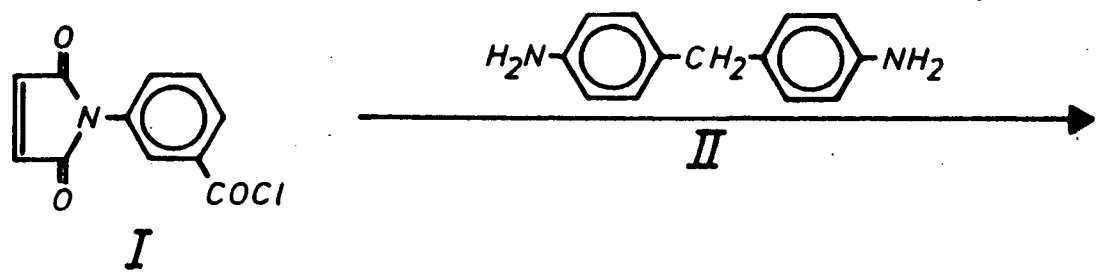
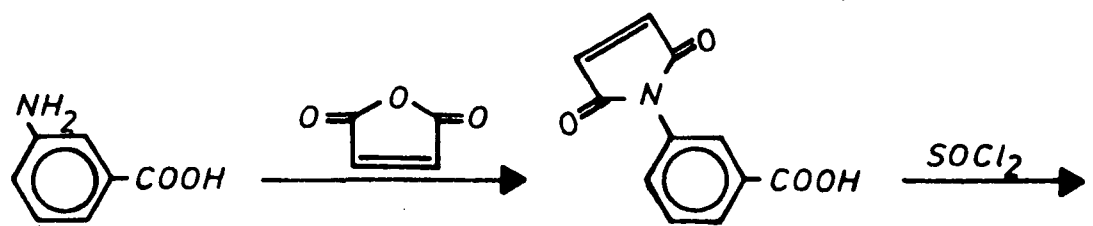


Figure 3: Chemistry of M 751 -resin

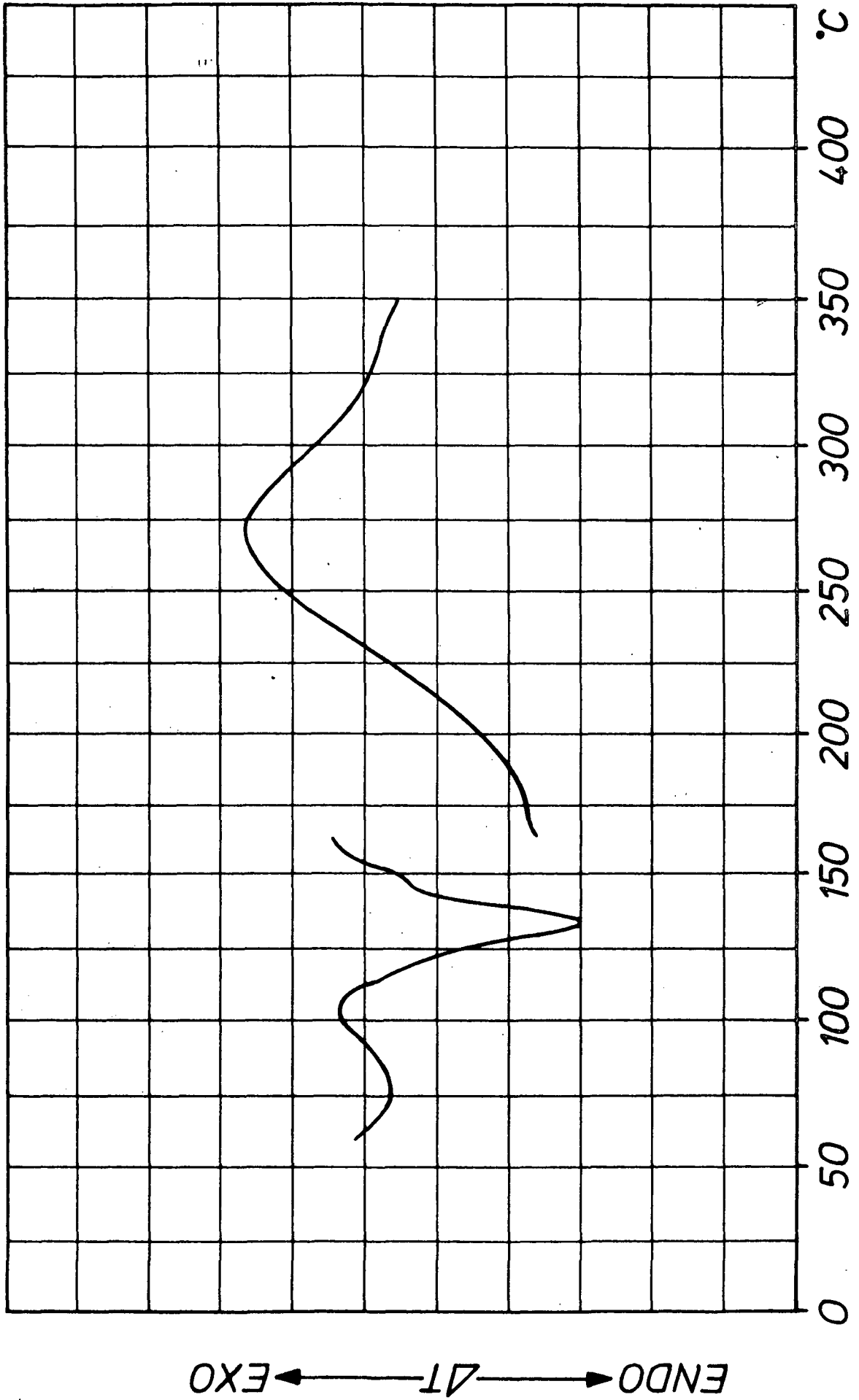


Figure 4: Melting and polymerization behaviour of bismaleimide resin M 751

Cam 11: 11/01/77

10 kg Delivery to NASA

REF. Al - pan

PROGRAM MODE Heat

RATE 10 °C MIN START °C

ORIGIN:

T

20 °C IN

SCALE SETTING

ΔT

0,5 °C IN

DATE 23.11.1977

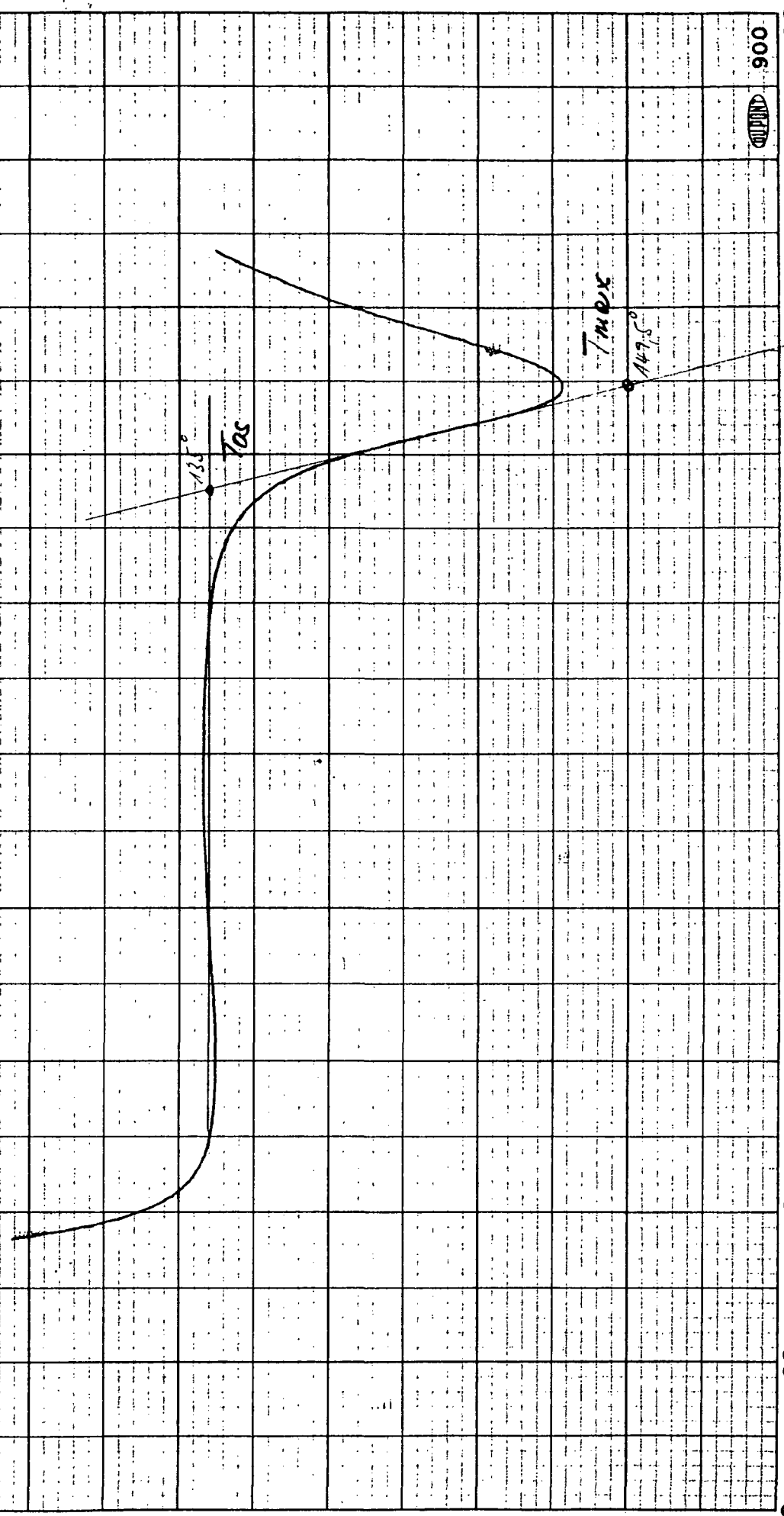
OPERATOR Stenzenberger

Figure 5:

EXO

ΔT

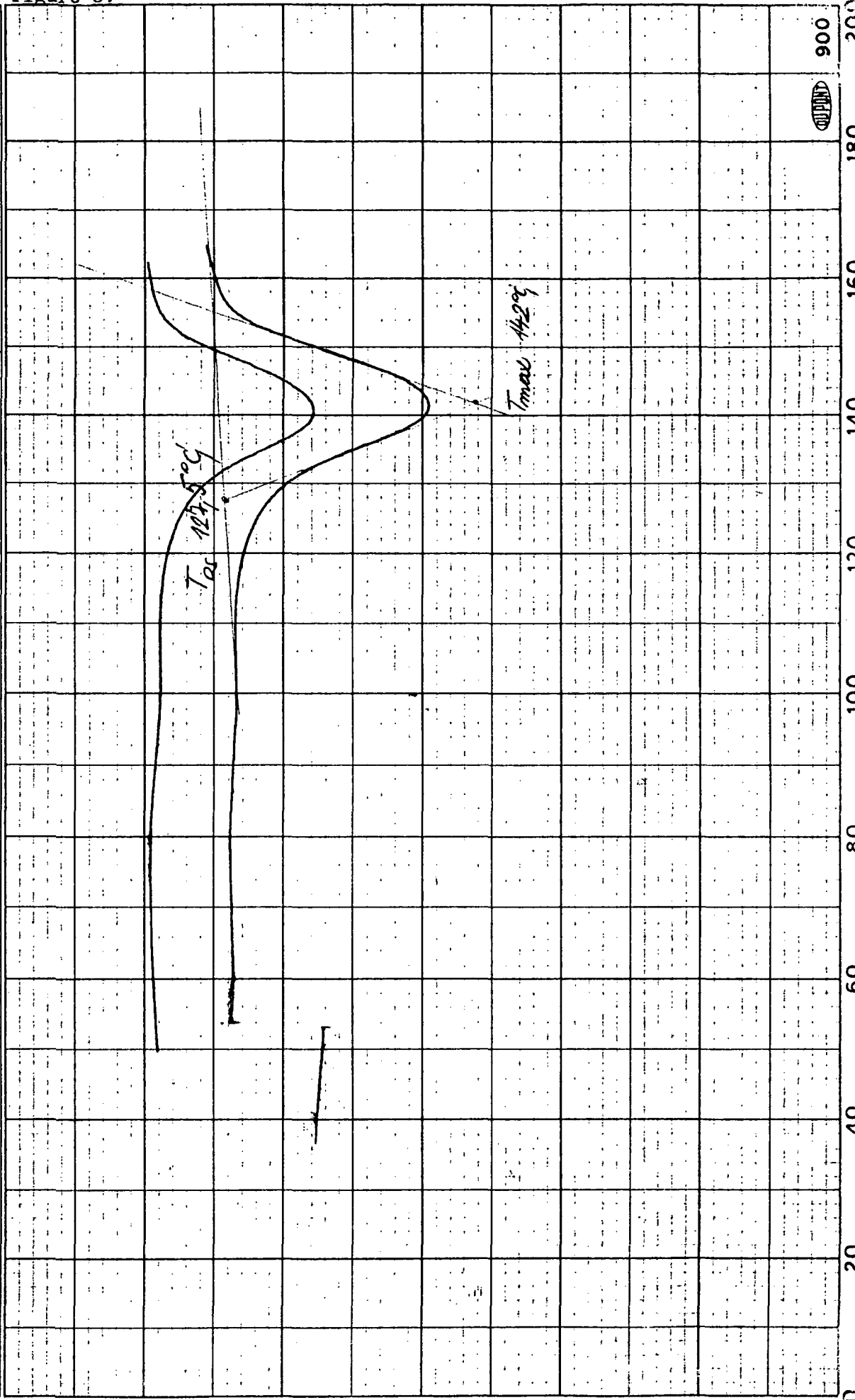
ENDO



STANDARD 11-11-1977

ORIGIN:	REF. AL - pan	DATE 3.2.1978	OPERATOR Stenzenberger
	PROGRAM MODE Heat		
	RATE 10 $\frac{^{\circ}\text{C}}{\text{MIN}}$. START $^{\circ}\text{C}$		
	SCALE SETTING		
	T	ΔT	
	20 $\frac{^{\circ}\text{C}}{\text{IN}}$	0.5 $\frac{^{\circ}\text{C}}{\text{IN}}$	

Figure 6:



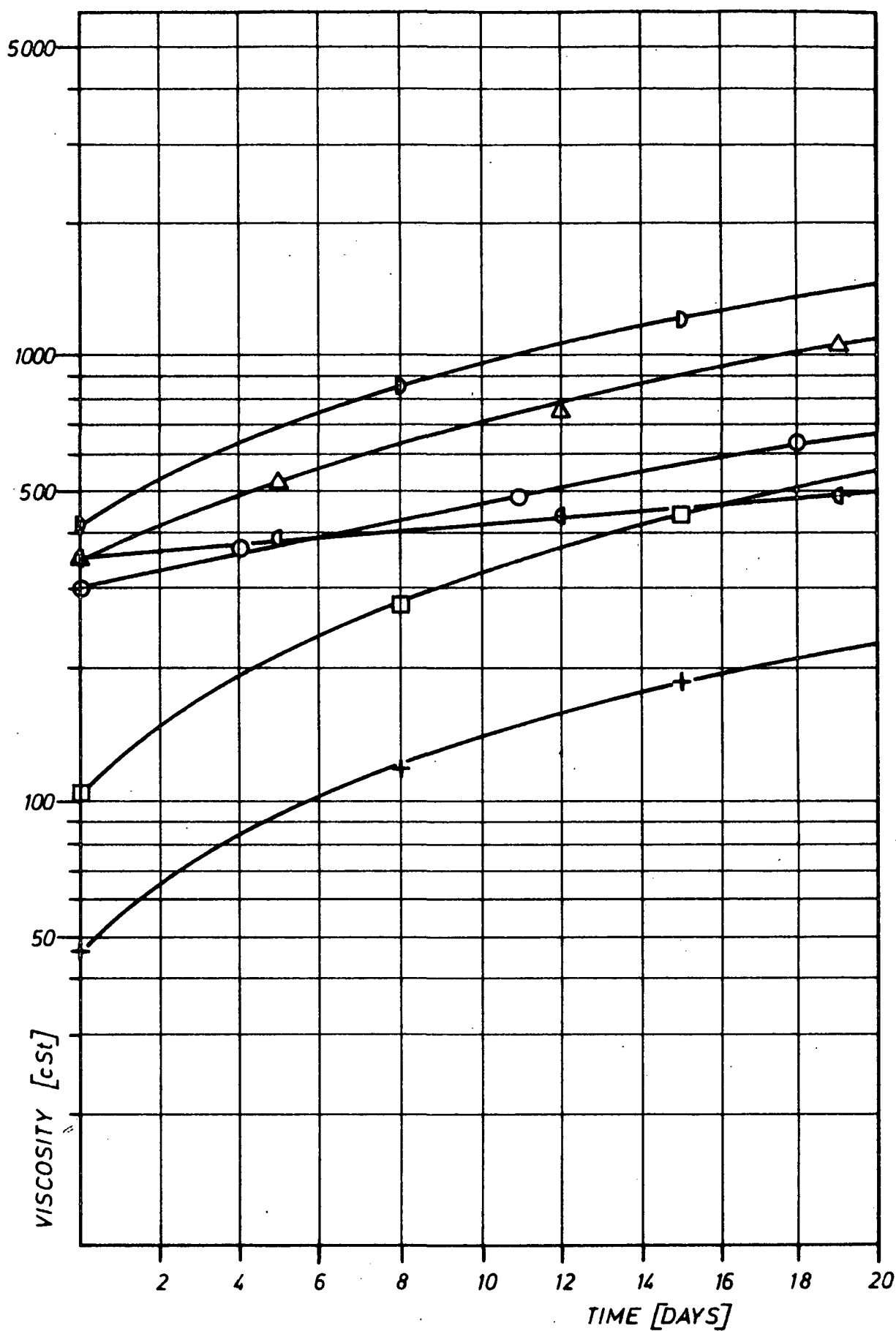


Figure 7: VISCOSITY-TIME profiles of M 751-resin solutions

- T4 in NMP 50%ig
- + T8 in DMF 50%ig
- Δ T9 in NMP 47%ig, aging at 20°C
- ◐ T9 in NMP 47%ig, aging at 4°C
- T8 in DMAc 50%ig
- D T8 in NMP 50%ig

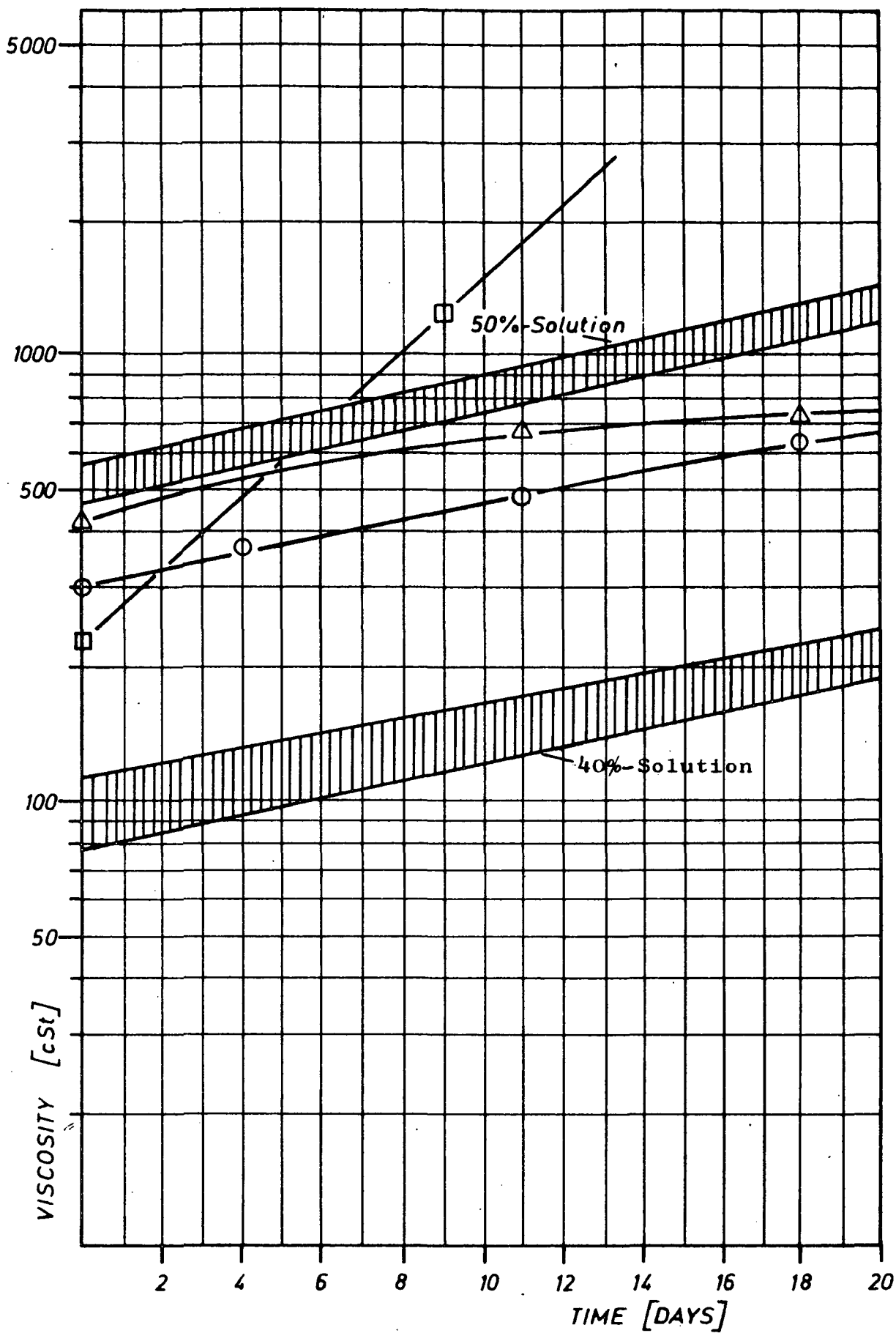


Figure 8: VISCOSITY-TIME profiles of M 751- and K 601-resin

Figure 9:

DRYING CURVES for M751/181 PREPREGS

○ DMAc, 140°C, dry resin content 34.43%

□ DMAc, 160°C, dry resin content 34.98%

△ DMAc, 180°C, dry resin content 34.55%

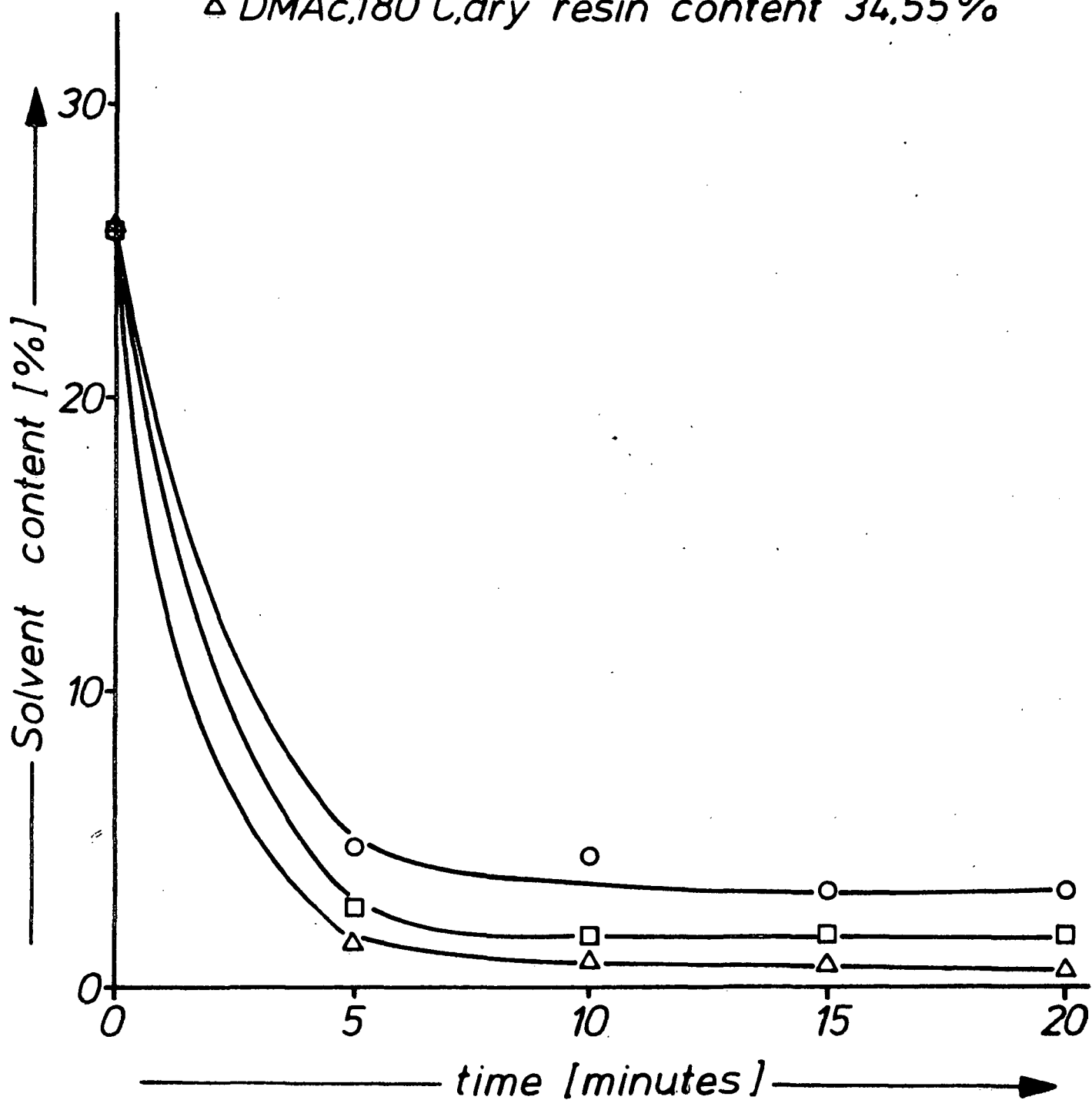
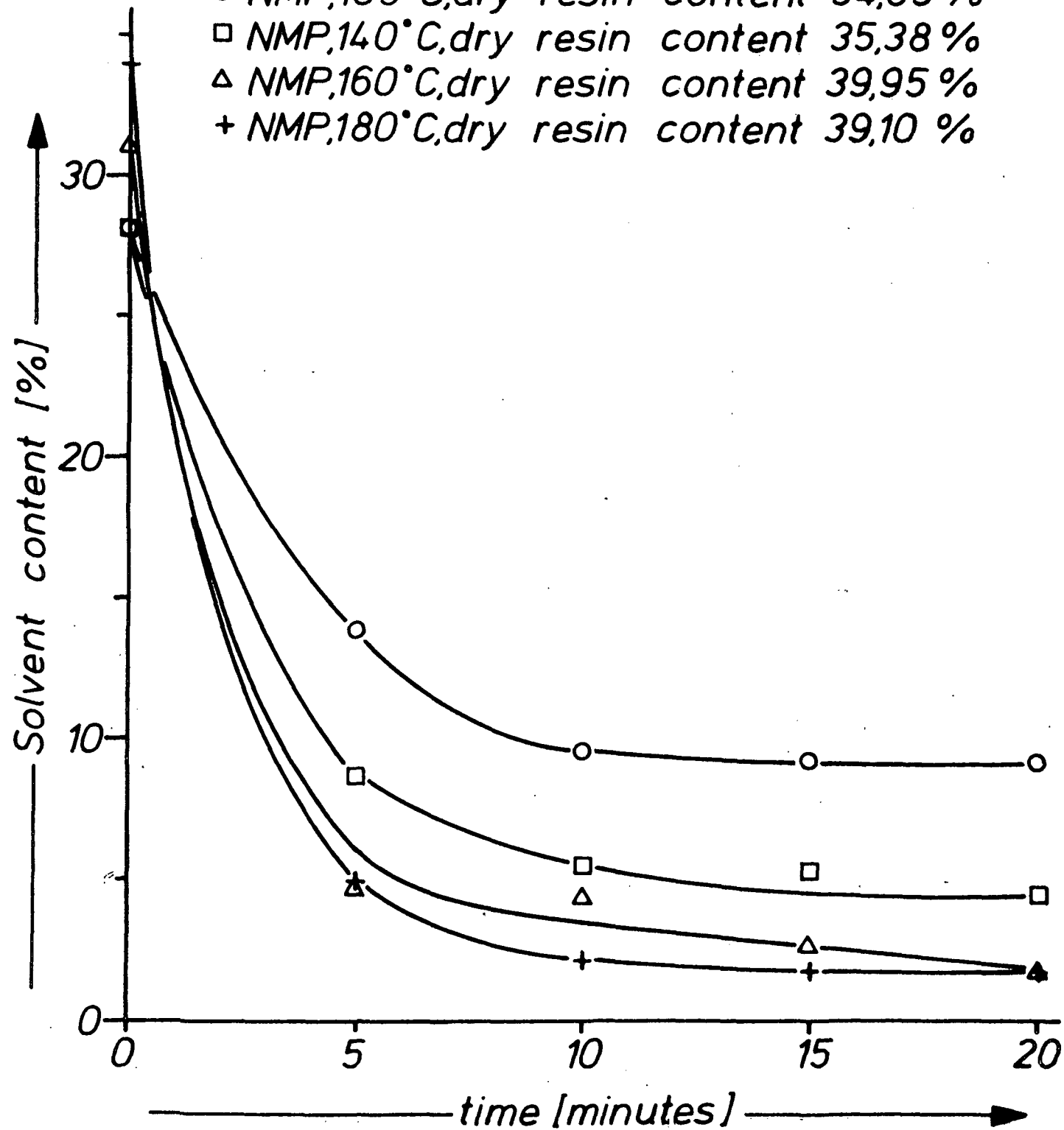


Figure 10:

DRYING CURVES for M751/181-PREPREGS

- NMP, 105°C, dry resin content 34,85 %
- NMP, 140°C, dry resin content 35,38 %
- △ NMP, 160°C, dry resin content 39,95 %
- + NMP, 180°C, dry resin content 39,10 %



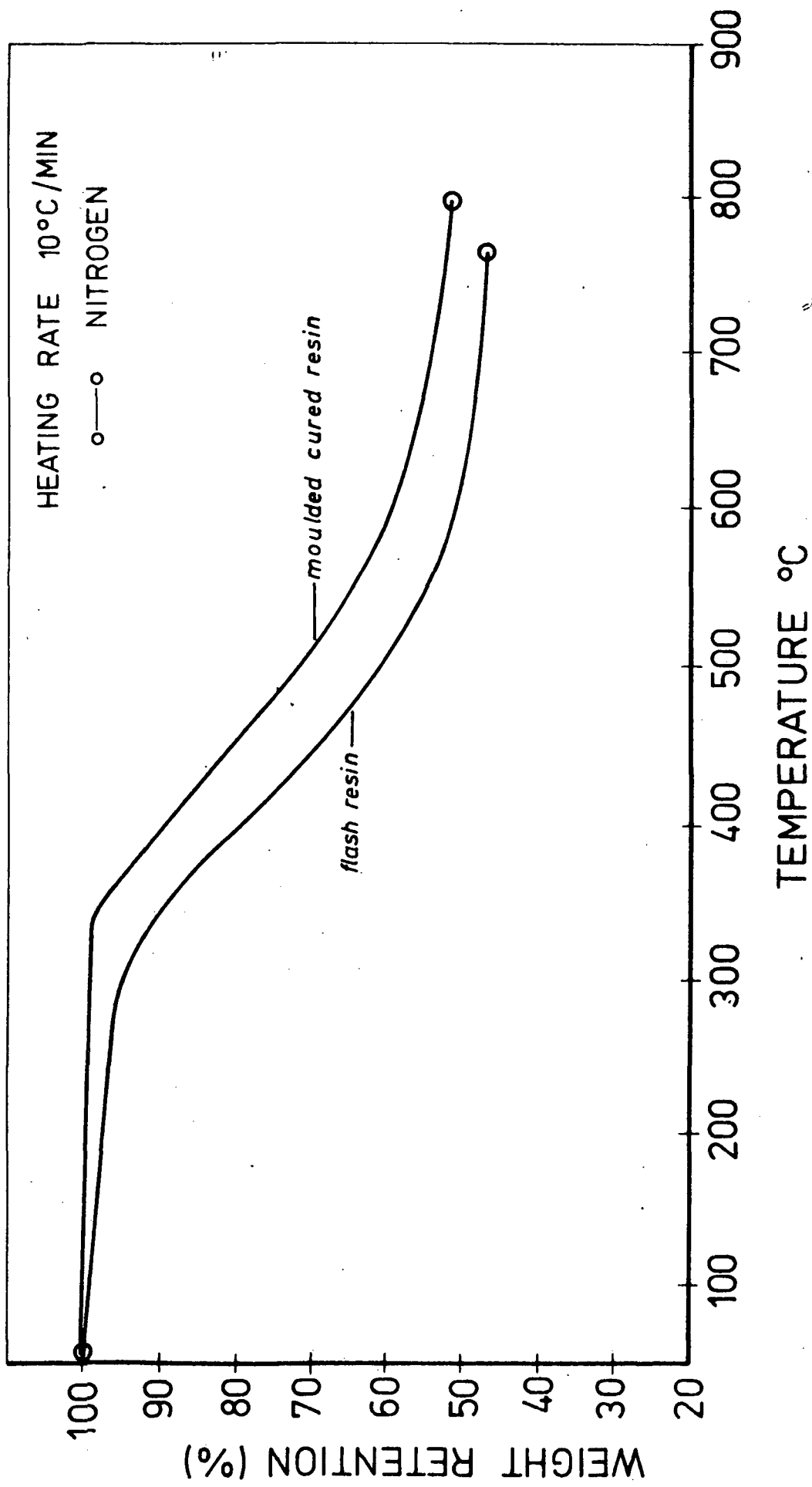


Figure 11: TGA - Thermograms of bismaleimide resin M 751

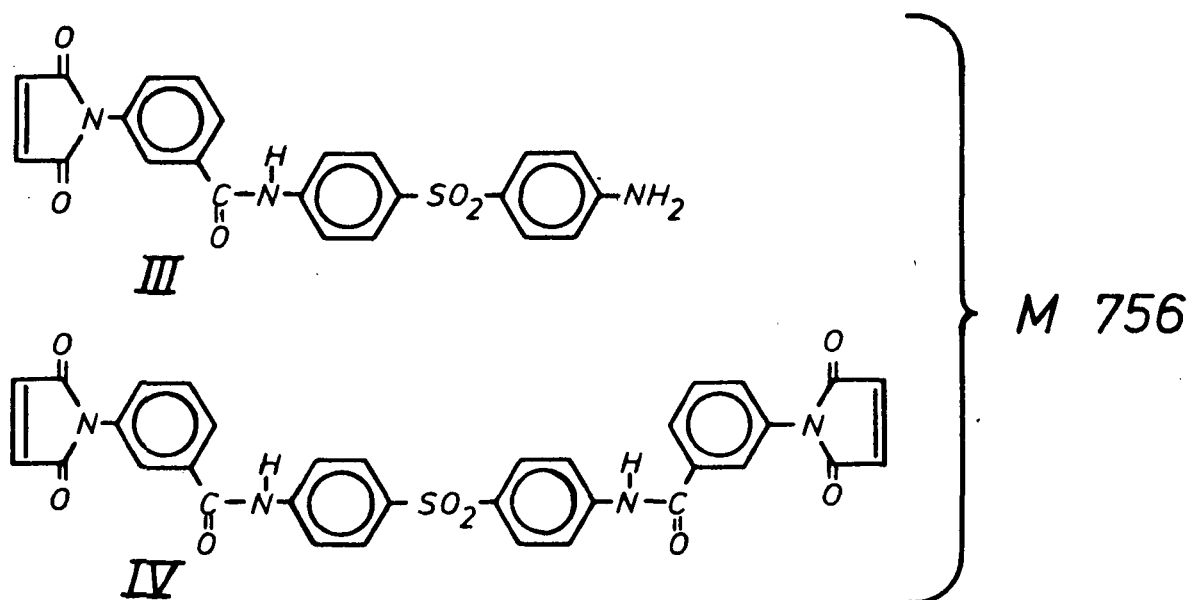
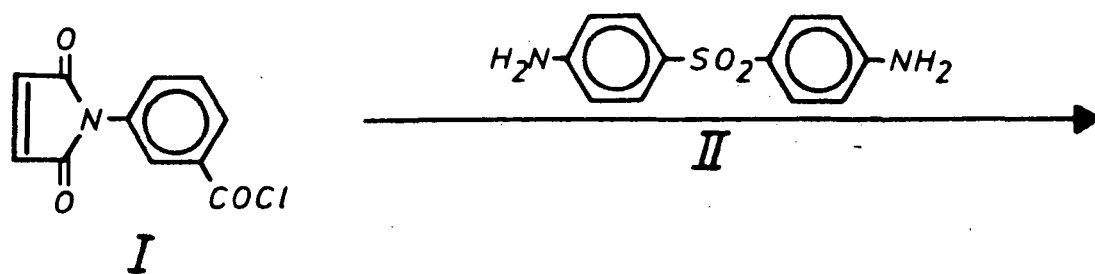
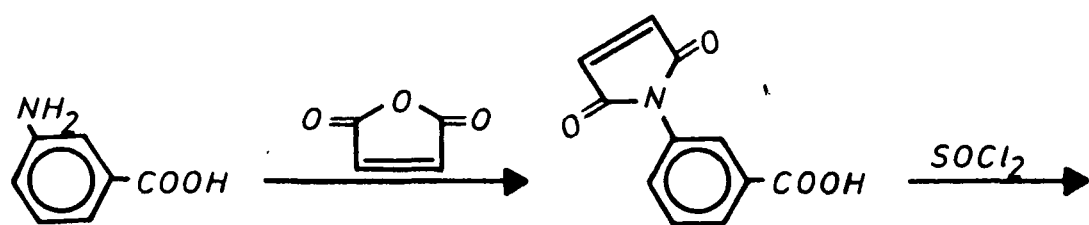
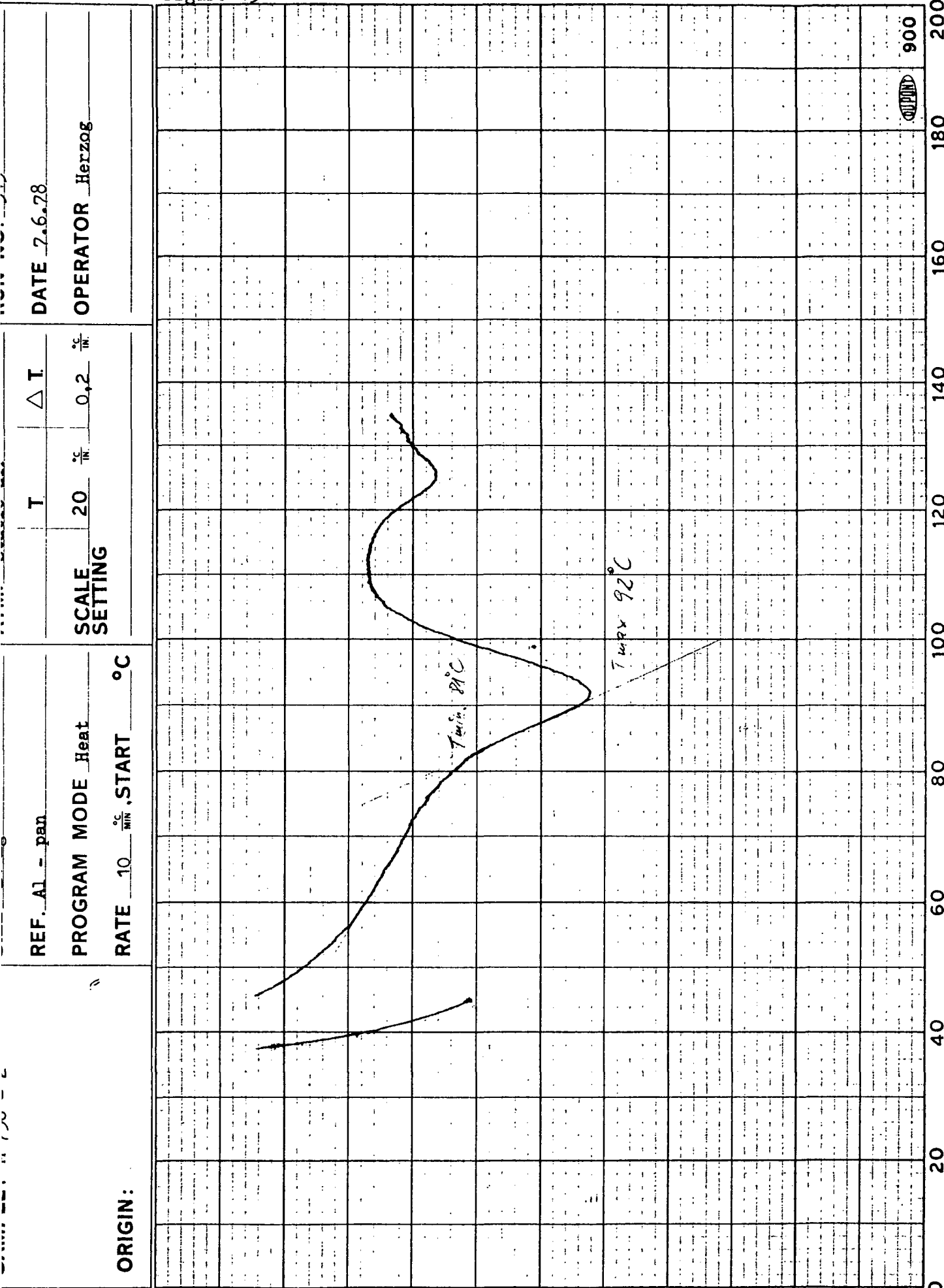


Figure 12: Chemistry of maleimide resin M 756

Figure 13:

(37)



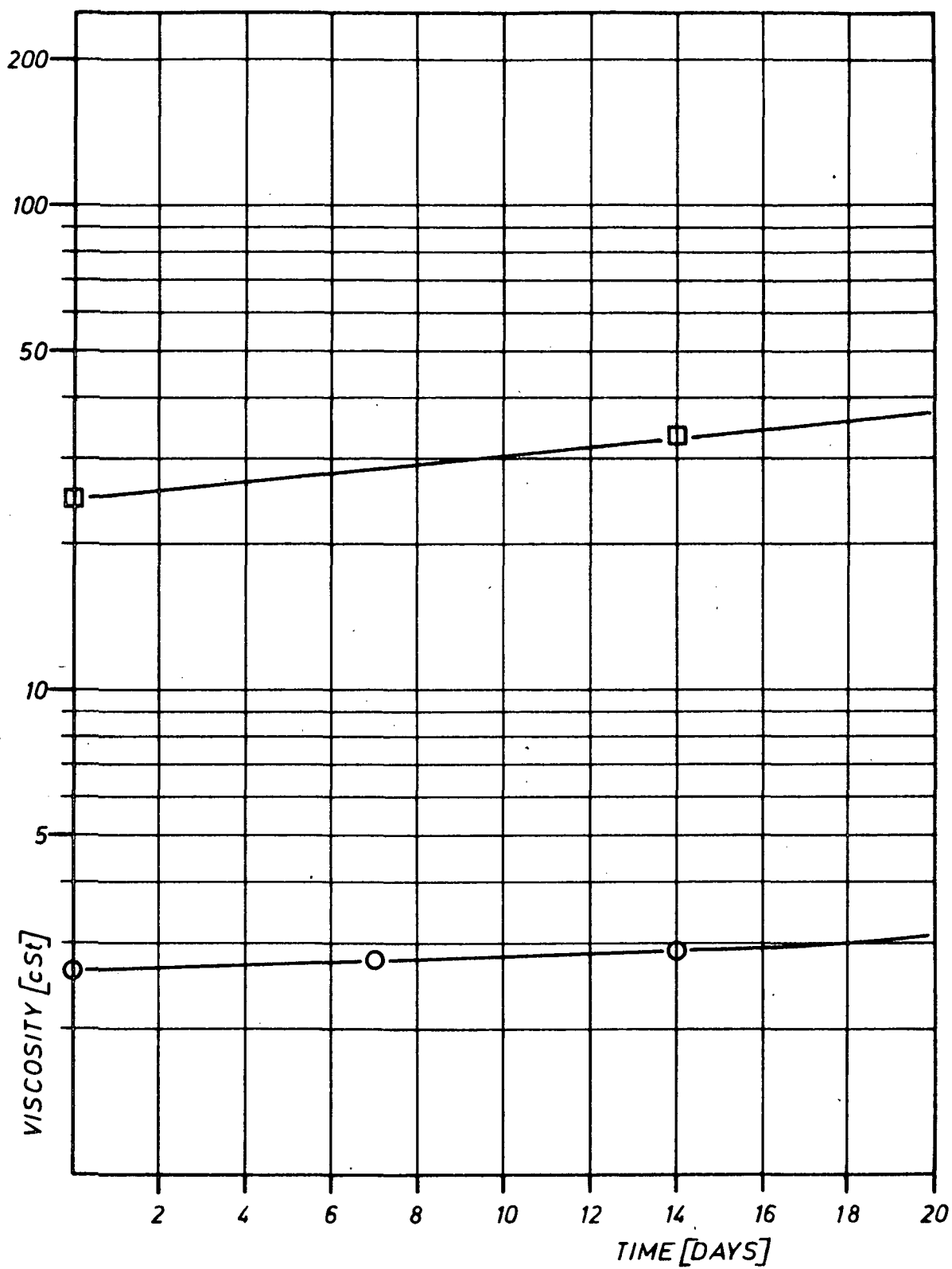


Figure 14: VISCOSITY-TIME profiles of M 756-2 resin solutions

○ 40% solution in Acetone
□ 50% solution in THF

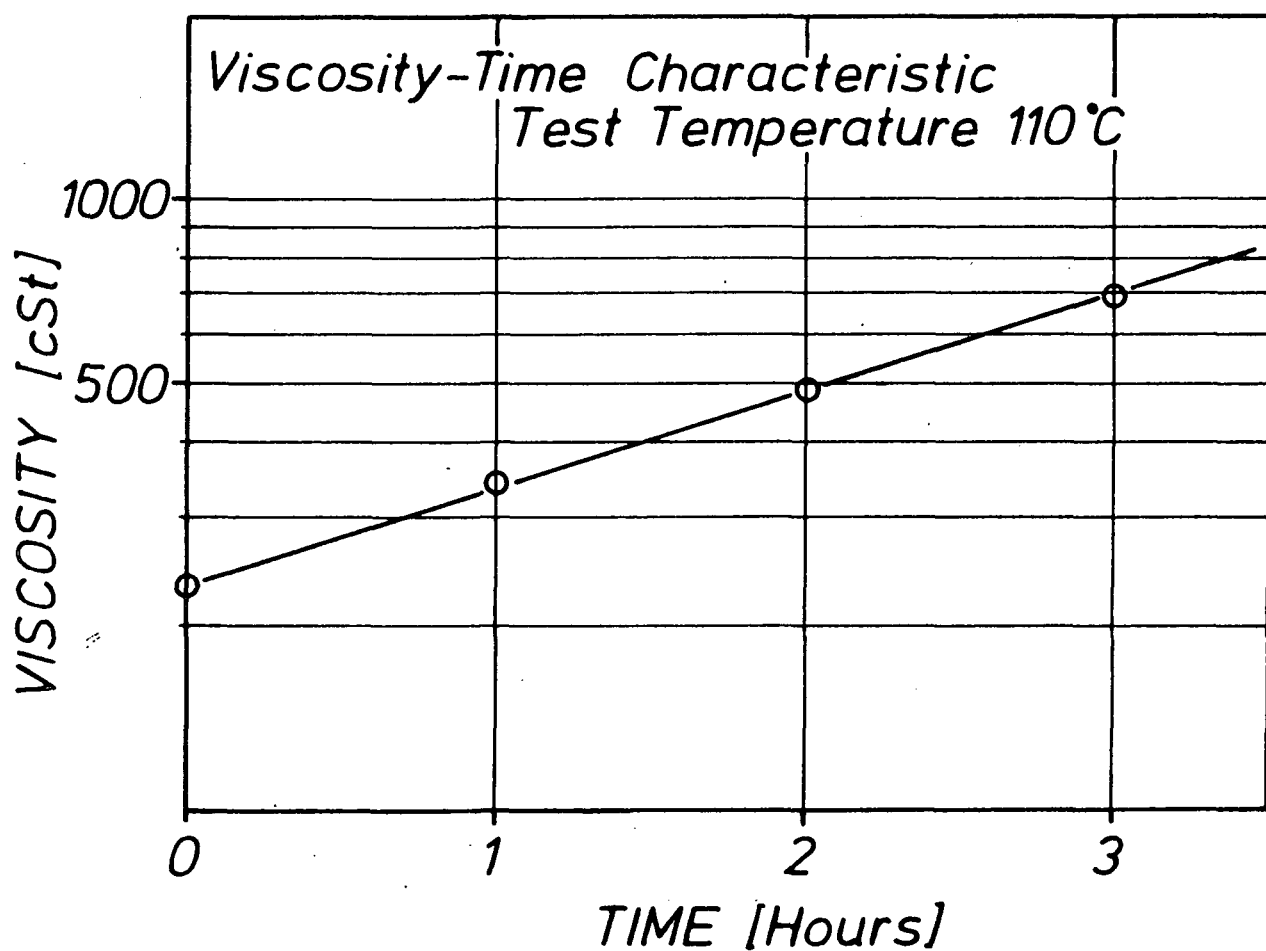
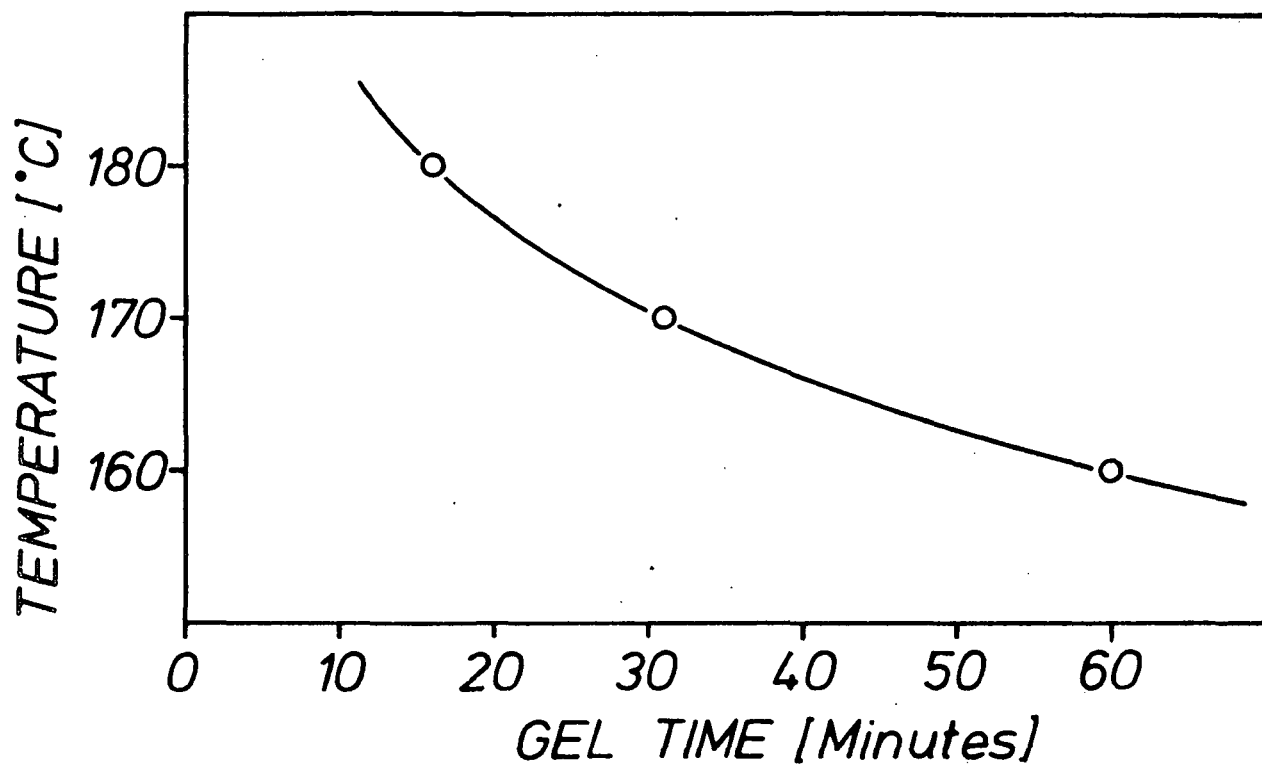
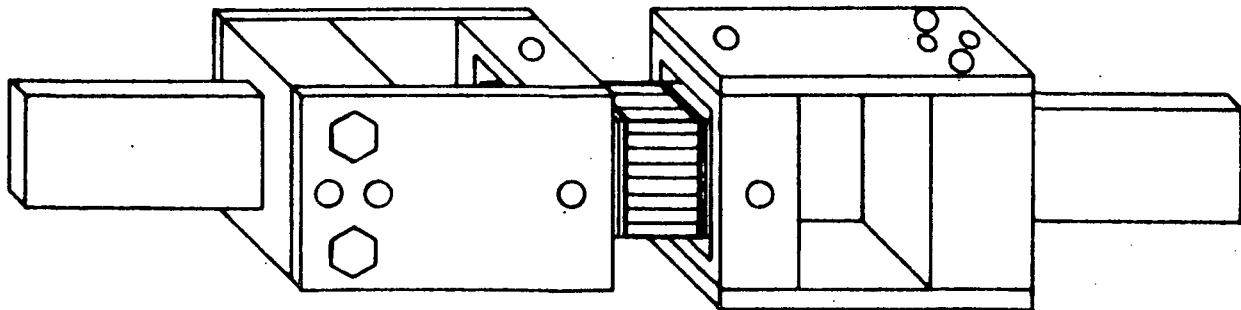


Figure 15: Hot melt bismaleimide resin Code C (batch M 1268)

TEST PROTOCOL FOR FLATWISE TENSILE
STRENGTH EVALUATION



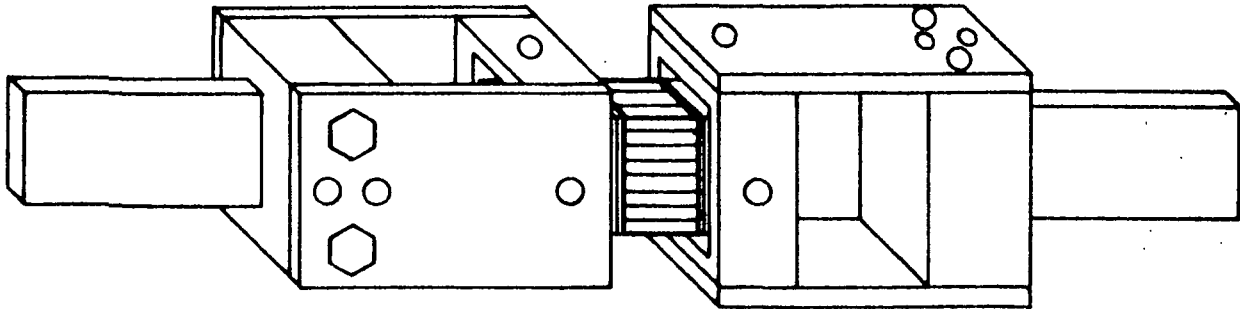
FLATWISE TENSILE STRENGTH OF SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N·cm ²	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,19	1930	210,01		Core + Bond	Nomex HXH10-1/8-3,0 Resin PBMI M 714 (45,3 %)	none
2	9,24	1815	196,43		Core		
3	9,23	1915	207,48		Core + Bond		
4	9,14	2090	228,67		Core		
5	9,15	2150	234,97		Core + Bond		
6	9,33	1715	183,82		Core + Bond		
7	9,12	2160	236,84		Core		
8	9,05	1890	208,84		Core		
9	9,17	2030	221,37		Core + Bond		

Average
Standard Deviation

214,27
17,80

TEST PROTOCOL FOR FLATWISE TENSILE
STRENGTH EVALUATION



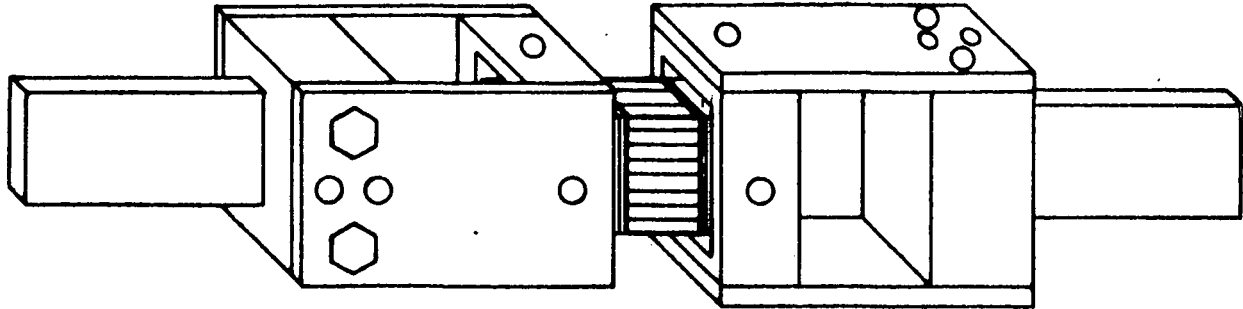
FLATWISE TENSILE STRENGTH OF SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength ² N.cm	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,29	2175	234,12		Core	Nomex HRR10-1/8-3,0	AF 126-2WT.06
2	9,25	2250	243,24		Core		
3	9,21	2080	225,84		Core		
4	9,31	2200	236,31		Core		
5	9,11	2185	239,85		Core		
6	9,25	2230	241,08		Core + Bond		
7	9,19	2100	228,51		Core + Bond		
8	9,28	2180	234,91		Core + Bond		
9	9,22	1450	(157,27)		Core + Block		

Average
Standard Deviation

235,48
6,04

TEST PROTOCOL FOR FLATWISE TENSILE
STRENGTH EVALUATION

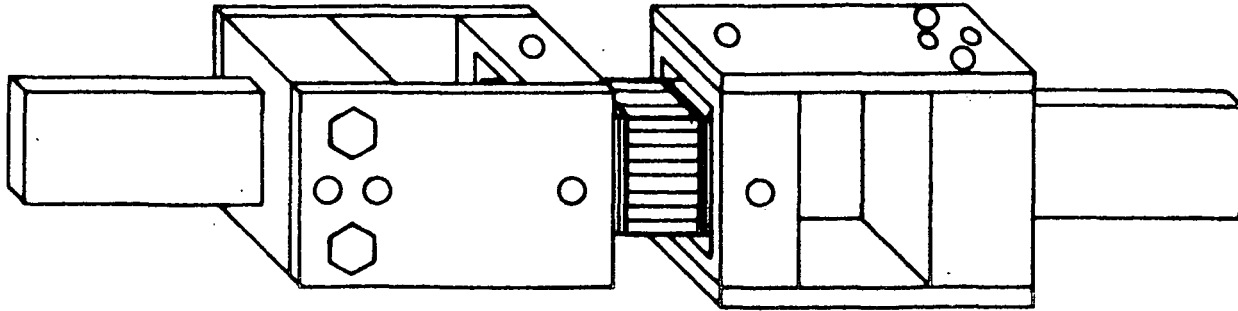


FLATWISE TENSILE STRENGTH OF SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N·cm ²	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,12	490	(53,73)		Loading Block	Nomex HRH10-1/8-3,0	AF 126-2WT.06
2	9,22	2050	222,34		Core		
3	9,12	1950	213,82		Core		
4	9,15	2000	218,58		Core		
5	9,07	1850	203,97		Core		
6	9,17	2060	224,65		Core		
7	9,20	240	(26,09)		Loading Block		
8	9,21	2000	217,16		Core		
9	9,15	2060	225,14		Core		

Average 217,95
Standard Deviation 7,41

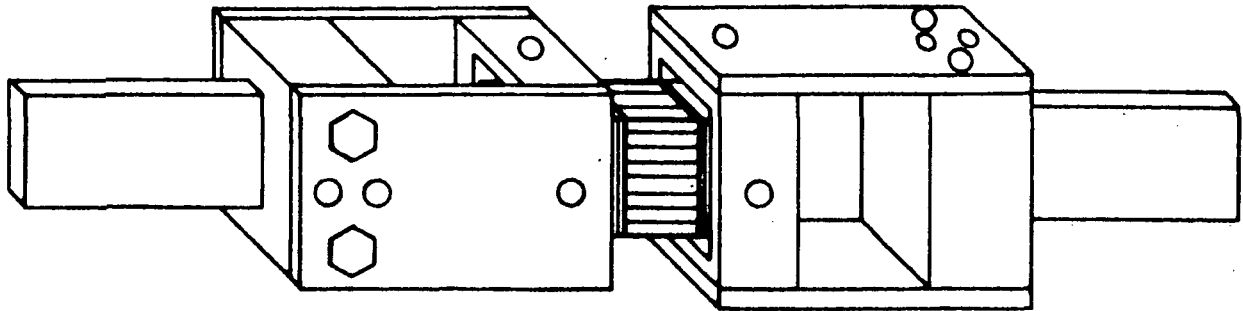
TEST PROTOCOL FOR FLATWISE TENSILE
STRENGTH EVALUATION



FLATWISE TENSILE STRENGTH OF SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N·cm	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,11	---	---		Loading Block	Nomex HRH10-1/8-3,0 Resin PBMI M 997 (29,5 %)	none
2	9,13	640	70,10		Bond		
3	9,18	200	21,79		Loading Block		
4	9,24	380	41,13		Bond + Block		
5	9,19	610	66,38		Bond		
6	9,17	530	57,80		Bond		
7	9,32	750	80,47		Bond		
8	9,16	670	73,14		Bond		
9	9,21	745	80.89		Bond		

Average 61,46
Standard Deviation 20,61

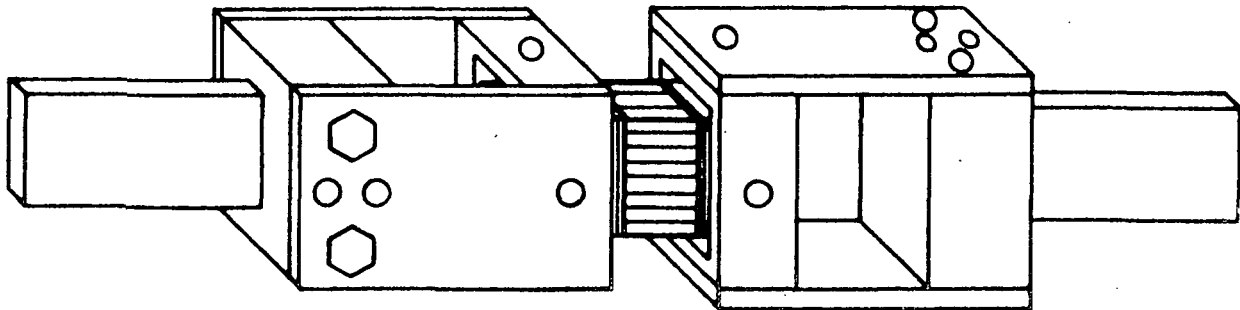


FLATWISE TENSILE STRENGTH of SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N·cm	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,12	650	71,27		Bond	Nomex HRH10-1/8-3,0 Resin PBI M 997 (37,1 %)	none
2	9,16	865	94,43		Bond		
3	9,12	875	95,94		Bond		
4	9,11	995	109,22		Bond		
5	9,13	915	100,22		Bond		
6	9,16	835	91,16		Bond		
7	9,12	1050	115,13		Bond		
8	9,13	730	79,96		Bond		
9	9,13	1120	122,67		Bond		

Average
Standard Deviation

97,78
16,34

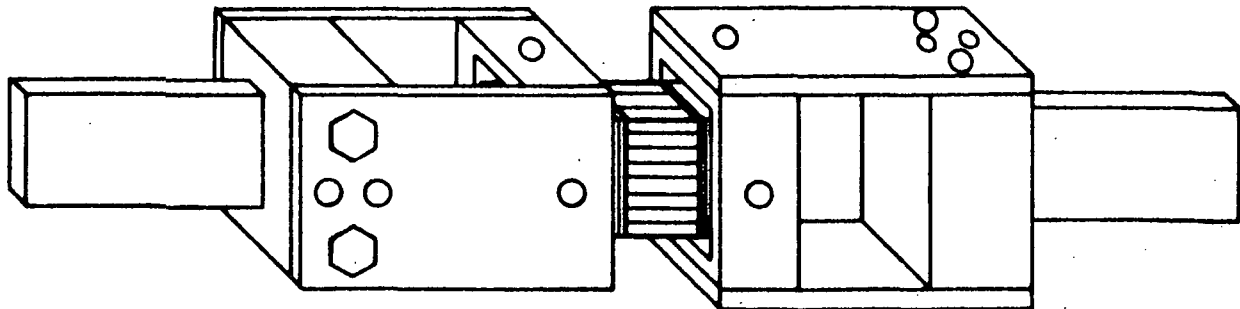


FLATWISE TENSILE STRENGTH of SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N·cm ²	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,12	1825	200,11		Bond	Nomex HHR10-1/8-3,0 Resin PEMI M 997 (37,9 %)	none
2	9,13	1640	179,63		Bond		
3	9,17	2040	222,46		Bond		
4	9,19	1840	200,22		Bond		
5	9,14	1900	207,88		Bond		
6	9,11	2030	222,83		Core		
7	9,13	1930	211,39		Core + Bond		
8	9,14	1820	199,12		Core + Bond		
9	9,14	2000	218,82		Core		

Average
Standard Deviation

206,94
13,94

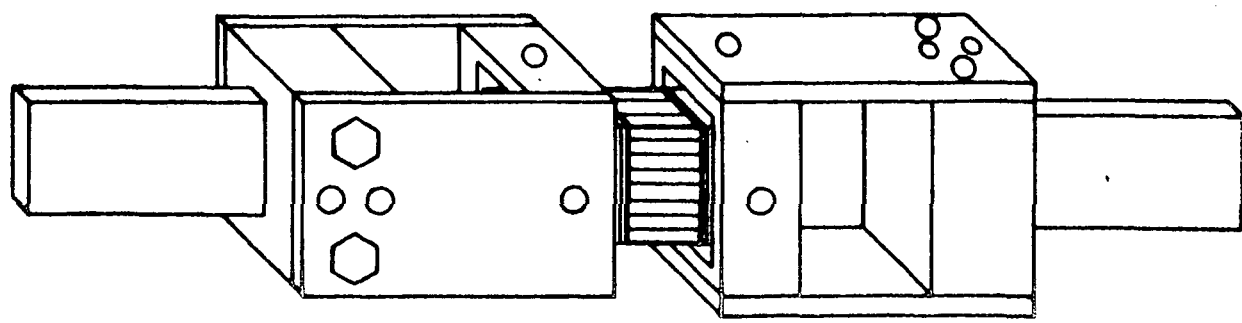


FLATWISE TENSILE STRENGTH OF SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N·cm ²	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,23	1700	184,18		Bond	Nomex HXH10-1/8-3,0 Resin PBM M 997 (37,9 %)	none
2	9,23	1640	177,68		Bond		
3	9,29	1780	191,60		Bond		
4	9,28	1850	199,35		Core		
5	9,29	1880	202,37		Core + Bond		
6	9,25	1690	182,70		Bond		
7	9,33	1860	199,36		Bond		
8	9,26	1880	203,02		Core + Bond		
9	9,29	1850	199,14		Core		

Average
Standard Deviation

193,27
9,53



FLATWISE TENSILE STRENGTH OF SANDWICH PANELS

Sample No.	Area cm ²	Force N	Tensile strength N.cm ²	desired tensile strength	Mode of failure	Honeycomb Type and thickness	Binder Primer
1	9,18	1790	194,99		Core	Nomex HXH10-1/8-3,0 Resin PBI M 997 (37,5 %)	none
2	9,19	1780	193,69		Core		
3	9,20	1840	200,00		Core		
4	9,18	1720	187,36		Core		
5	9,22	1830	198,48		Core		
6	9,24	2000	216,45		Core		
7	9,28	1980	213,36		Core		
8	9,30	1770	190,32		Core		
9	9,25	2130	230,27		Core		

Average

202,77

Standard Deviation

14,22